











AN ADVANCED COURSE OF INSTRUCTION  
IN  
CHEMICAL PRINCIPLES



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AN ADVANCED COURSE OF INSTRUCTION  
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CHEMICAL PRINCIPLES

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## PREFACE

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IN this book are presented the results of the authors' many years' experience with their own classes in the development of a thorough course of instruction in the laws and theories of chemistry from quantitative stand-points. The course is intended for junior, senior, or graduate students of physical chemistry in colleges, scientific schools, and universities, who have completed the usual freshman and sophomore courses in chemistry, physics, and mathematics.

The purpose of the course is to give such students an intimate knowledge of fundamental chemical principles and a training in logical, scientific thinking, such as will enable them to attack effectively the practical problems arising in their subsequent educational or professional work in any of the branches of chemistry or related sciences. Descriptive text-books of physical chemistry afford a general survey of chemical laws and theories which may suffice for the purposes of students who are not preparing for a professional career on the educational, research, or industrial sides of chemistry, but they do not give that intensive training which is essential for pursuing successfully more specialized courses of scientific study or for applying chemical principles to industrial problems. No one regards a course of lectures on the principles of mathematics as a suitable method of giving beginners the ability to handle that science, and with scarcely more reason can descriptive courses on physical chemistry be expected to afford a working knowledge of chemical principles in their quantitative aspects. Only by constantly applying the principles to concrete problems will the student acquire such a knowledge and the power to use it in new cases.

Accordingly, the course of instruction is so planned as to make the student think about the significance of the principles presented and work out for himself the method of treatment of special cases upon the basis of those principles. To this end, the text is interspersed with problems, which prevent the student from memorizing the principles or complacently believing that a formal knowledge constitutes a real understanding of them. These problems are for the most part not of the usual type, involving merely substitution in formulas and mathematical operations, but are such as require clear logical thinking in the application of the principles to the cases under consideration. They are not merely supplementary or incidental to the text, but they are the feature about which the whole presen-

tation centers. The aim striven for has been to make each problem serve a definite purpose, and to have it involve independent thought, yet in such measure as shall not be beyond the mental capacity of college students who have completed good general courses in mathematics, physics, and chemistry. The problems have been gradually developed as a result of many years' trial of the plan with large classes of such students. While the authors realize that the presentation is in its details still far from perfect, they have decided to defer publication of it no longer, in the hope that this educational method, novel in this subject, may be further developed through the experience of other teachers, from whom suggestions will be gratefully received.

In order to attain the purpose in view and yet keep the book within the limits of an undergraduate course, the subjects treated have been carefully selected from the point of view of their practical importance to the chemist; many topics being omitted that are commonly included in descriptive courses on physical chemistry or in complete treatises on the subject. The book consists mainly, as the table of contents shows, in a development of the atomic, kinetic, and ionic theories through a consideration of the physical properties directly related to them, and in a treatment, with the aid of these theories, from mass-action, phase, and thermodynamic view-points, of the principles relating to the rate and equilibrium of chemical reactions. The newer theories of atomic structure and of radiation have been reluctantly omitted; because, in spite of their transcendent interest and their importance to the future of chemistry, in their present stage of development they are appropriately treated in an advanced course of the research type, rather than in a fundamental undergraduate course of a systematic character. Lack of time has led also to the omission of those more specialized parts of the subject that treat of the physical properties of substances in the various states of aggregation, such as the metallic, crystalline, liquid, and dispersed states; for, important as are some of the generalizations already arrived at in these fields, their inclusion in this course would have involved sacrifice of an adequate and intensive treatment of the more fundamental principles. A systematic notation (summarized on page 297) has been employed throughout the book.

The course of instruction, as carried out by the authors, consists of class-room exercises, mainly of the recitation type, given to sections of twenty to thirty students. At each exercise a number of problems are assigned which are to be solved and handed in at the beginning of the next exercise; the students being advised to use slide-rules so as to shorten the arithmetical work. The instructor then solves these problems on the blackboard, questioning members of the class as to how he shall proceed. He emphasizes the principles involved and the best way of looking at the problems under consideration. In the assignments it is customary not to

give out all at once the whole group of problems following a section of the text, but to assign only the first one or two of such a group, together with the last problems of the preceding group. This enables the instructor to discuss the principles relating to a new group of problems after the students have given some thought to them, but before they have passed to another topic; thereby insuring a better understanding of the general view-point from which it is best to attack the problems and removing difficulties which individual students may experience. Frequent written tests are given, consisting of review problems different from those already solved by the class, but involving the same principles.

In order that the student may better appreciate the principles he is studying, it is desirable that the class work be accompanied by a brief laboratory course, or if that is not practicable by lecture experiments, whose primary purpose should be to give concrete illustrations of the nature of the basic phenomena under consideration (such as vapor-pressure, ion-migration, reaction-rate); for the experimental methods by which the properties are determined are not described in this book, except in so far as these are essential to an understanding of the phenomena. Moreover, no attempt has been made to present the historical and research aspects of the topics, because of the impossibility of doing this at all adequately in a brief systematic treatment of the well-established principles of the subject. Many teachers will doubtless desire to supplement this systematic presentation by mentioning these historical and research aspects, and by suggesting the collateral reading of reviews and original articles that have appeared in chemical periodicals, or of text-books of physical chemistry in which these aspects are more fully discussed.

To cover satisfactorily the whole subject as here presented requires from 120 to 150 exercises; but, in order to make it readily adaptable to a one-year 90-hour course, certain articles and problems which are less important or more difficult are indicated by asterisks. It is also suggested that, when the subject must be completed in a one-year course, no attempt be made to include the thermodynamic treatment presented in Chapters X-XIII, but that, after taking up the chapter on thermochemistry, the course be completed by considering (without reference to its thermodynamic derivation) the applications of the important van't Hoff equation, as presented in Arts. 167-169. When the course extends through a year and a half, the second year work will naturally consist of Chapters IX-XIII, these constituting a systematic course on thermodynamic chemistry, which indeed may be pursued as a graduate subject by those who have not studied the earlier chapters of the book.

The authors desire to express their indebtedness to many of their colleagues for valuable suggestions, and especially to Professors S. J. Bates and E. B. Millard, and to Mr. Roger Williams, who have furnished detailed lists

of corrections and general criticisms. The authors desire also to thank Drs. G. N. Lewis and Merle Randall for the privilege of including, in advance of its publication in their book on Thermodynamics and the Free Energy of Chemical Substances, a table showing the values of the electrode-potentials recently derived by them.

*Pasadena and Cambridge, March, 1922.*

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## PART I

THE ATOMIC, MOLECULAR, AND IONIC THEORIES  
AND THE PROPERTIES OF SUBSTANCES DI-  
RECTLY RELATED TO THESE THEORIES



## CHAPTER I

### THE COMPOSITION OF SUBSTANCES AND THE ATOMIC THEORY

---

**1. The Field of Chemistry. Its General Principles the Subject of this Course.** — *Chemistry* treats of the composition and molecular structure of substances, of their properties in relation to their composition and molecular structure, of changes in their composition, and of the effects attending such changes. *Physics* treats of the properties of substances without relation to their composition, and of changes in state that do not involve changes in composition.

This course on *Chemical Principles* is devoted to a consideration of the more important general principles which express the properties and reactions of chemical substances. The subject here considered is sometimes called *general*, *theoretical*, or *physical chemistry*. The last of these names, which is now most commonly employed, carries the unfortunate implications that the subject is a separate branch of chemistry coördinate with inorganic, organic, analytical, or applied chemistry, and that it deals mainly with the physical sides of chemical science; whereas, in reality, it deals with the principles common to all branches of chemistry and is concerned primarily with purely chemical phenomena, such as the properties of substances in relation to their molecular structure, and such as the rate and equilibrium of chemical reactions and the attendant effects. The general plan adopted for the presentation of the subject in this book may be seen by reference to the headings of the Parts and Chapters in the Table of Contents given on the preceding pages.

**2. Pure Substances and Mixtures, Elementary and Compound Substances, the Elements, and the Law of Definite Proportions.** — Out of the materials occurring in nature there can be prepared substances which, when subjected to suitable processes of *fractionation* (that is, to operations which resolve the materials into parts or fractions), always yield fractions whose properties are identical when measured at the same pressure and temperature. Such substances are called *pure substances*; other substances which can be resolved by such processes into fractions with different properties being called *mixtures*. For example, whether a solid material is a pure substance or mixture

may be determined by partially melting or vaporizing it or by partially dissolving it in solvents, and by comparing the value of the density, melting-point, or some other sensitive property, of the unmelted, unvaporized, or undissolved part with that of the original material.

The fundamental idea involved in the preceding considerations is that there exists an order of substances, called pure substances, of relatively great stability toward resolving agencies, each one of which has a perfectly definite set of properties, sharply differentiated from those of other pure substances; so that there is not a continuous series of pure substances whose properties pass over into one another by insensible gradations.

Nearly all pure substances, called *compound substances* because of the behavior to be now mentioned, can be converted, by subjecting them to sufficiently powerful resolving conditions, into a small number of other pure substances, called *elementary substances*, which are not further decomposed by chemical or physical processes. In correspondence with this fact all substances are considered to be composed of a small number of kinds of matter, about ninety in all, called the *elements*; each elementary substance consisting of only one of these elements, and each compound substance of two or more of them.

Although some elements, those contained in the so-called radioactive substances, have been found to be undergoing spontaneous disintegration, elementary substances obviously constitute a separate order of substances of very great, but not unlimited, stability toward decomposing agents.

The general principle of the definiteness of the properties of pure substances applies also to the elementary composition of pure substances. This fact is expressed by the *law of definite proportions*, which states that a pure substance, however it be prepared, always contains its elements in exactly the same proportions by weight.

**3. The Law of Combining Weights.** — To the various elements definite numerical values can be assigned which when multiplied or divided by small whole numbers accurately express the weights of the elements which are combined with one another in all pure substances. Such numerical values are called the *combining weights* of the elements. Adopting 16 as the combining weight of oxygen, the combining weight of any other element may be defined to be that weight of it which combines with 16 parts of oxygen, or with a quantity of oxygen (such as 8, 24, or 32 parts) which stands to 16 in the ratio of small whole

numbers. It will be seen from this definition that a combining weight is an arbitrary multiple of an exact quantity. The principle that the composition of all pure substances can be accurately expressed in terms of the so-defined combining weights of the elements is called the *law of combining weights*.

*Prob. 1. — The Concept and Law of Combining Weights. — a.* Two oxides of sulfur are found by analysis to contain 50.05% and 40.04% of sulfur. Derive from these analytical results two values for the combining weight of sulfur, and show that these values stand to one another in the ratio of small whole numbers. *b.* Derive a combining weight for iron from the fact that one of its oxides contains 30.06% of oxygen. *c.* Derive another value for the combining weight of iron from the fact that one of its sulfides contains 36.47% of sulfur, whose combining weight was found in *a*; and show that the two values of the combining weight of iron stand to each other in the ratio of small whole numbers.

**4. The Atomic Theory.** — The fact that elements combine with one another only in the proportions of their combining weights or multiples of them originally suggested the following fundamental *atomic* and *molecular hypotheses*:

(1) The matter constituting each element is made up of extremely small particles, called *atoms*, which are alike in every respect, and which are not subdivided in ordinary chemical or physical changes; there being as many different kinds of atoms as there are elements.

(2) The atoms associate with one another, usually in small numbers, forming a new order of distinct particles, called *molecules*. Pure substances usually consist of only one kind of molecule, while mixtures always contain two or more kinds; and the molecules of elementary substances consist of atoms of the same kind, while those of compound substances consist of atoms of different kinds.

By supplementing these hypotheses with certain other hypotheses, developing them to their logical conclusions, and applying these conclusions to physical and chemical phenomena, many of the physical properties and chemical reactions of substances have been explained. Indeed, the adequacy of the fundamental hypotheses has now been confirmed in so many ways that there is no longer any doubt that substances are really made up of atoms and molecules of substantially the assumed character.

These hypotheses and the conclusions drawn from them constitute the *atomic* and *molecular theories*; the former term being commonly

used when properties that are more directly related to the characteristics of the atoms or to the atomic structure of the molecule are under consideration; the latter term when properties that are determined primarily by the characteristics of the molecule as a whole are being studied.

A substance which contains only a single kind of molecule is called a *chemical substance* (or by some authors a molecular species). Pure substances normally consist of single chemical substances; but they may consist of two or more chemical substances which are capable of conversion into one another and which are always present in definite proportions at any given temperature and pressure in consequence of the rapid establishment of equilibrium between them. Thus, the pure substance liquid water contains the two chemical substances whose molecules are  $\text{H}_2\text{O}$  and  $\text{H}_4\text{O}_2$ , these being always present in definite proportions at any given temperature and pressure, since equilibrium is almost instantaneously established between them; but the pure substance water-vapor at small pressures is a single chemical substance, for it contains only molecules of the form  $\text{H}_2\text{O}$ . Pure substances which, like water, water-vapor; and ice, are converted into one another by changes of pressure and temperature, are commonly spoken of as the same substance; but they may consist of different chemical substances, as has just been illustrated.

The relative weights of the atoms of the various elements and of the molecules of the various substances are called their *atomic weights* and *molecular weights*, respectively; and as a standard of reference, the weight of the oxygen atom taken as 16 is adopted.

The atomic theory evidently requires that the weights of elements that combine with one another be proportional to the weights of their atoms or to multiples of those weights; in other words, that the atomic weights be equal to the combining weights or to multiples of them.

**5. Determination of Combining and Atomic Weights.** — The determination of the atomic weight of an element involves two distinct steps: (1) the determination of its combining weight; and (2) the determination of that multiple of its combining weight which is its atomic weight.

The combining weight of an element is experimentally determined by preparing one of its compounds or the elementary substance itself in a state of the highest possible purity, and completely converting it into another pure substance, the other elements contained in the sub-

stances being of known combining weights. The quantities of the initial substance taken and of the final substance obtained are accurately weighed, and from the ratio of these weights the combining weight is calculated. For example, the combining weight of hydrogen has been determined by burning a weighed quantity of pure hydrogen gas with oxygen and weighing the water formed; also by finding the weight of the oxygen consumed. Values for the weight ratios  $H_2 : H_2O$  and  $H_2 : O$  were thus established, and from each of them the combining weight of hydrogen was computed. The following problem illustrates the methods of determining combining weights in general, and it shows some of the fundamental determinations on which our present system of atomic weights is based.

*Prob. 2. — Determination of Combining Weights.* — Determine the exact combining weights of silver, potassium, and chlorine from the following data: In a series of eight experiments 801.48 g. of pure potassium chlorate were ignited or treated with hydrochloric acid, yielding 487.66 g. of potassium chloride. In another series of five experiments 24.452 g. of pure potassium chloride were dissolved in water and precipitated with silver nitrate, whereby 47.013 g. of silver chloride were obtained. In a third series of ten experiments 82.669 g. of pure silver were dissolved in nitric acid and precipitated with hydrochloric acid, yielding 109.840 g. of silver chloride.

*Ans.* Ag, 35.978  $x$ ; Cl, 11.825  $y$ ; K, 13.038  $z$ ; where  $x$ ,  $y$ , and  $z$  are ratios of whole numbers not determinable by gravimetric methods.

The multiple of the analytically determined combining weight which is the most probable atomic weight of each element was originally derived for most of the elements from theoretical principles relating to certain physical properties, especially the pressure-volume relations of gaseous compounds, the heat-capacities of the elementary substances in the solid and gaseous states, and the isomorphism of corresponding compounds of different elements in the crystalline state. The principles relating to the first two of these properties and their applications to atomic weight determinations are considered in Chapters II and IV. The system of atomic weights so derived finds its chief justification, however, in the fact that it has led to molecular formulas of chemical substances which represent their chemical behavior in a remarkably satisfactory manner. It has also led to the formulation of the periodic system of the elements, which affords a qualitative representation of many of the physical and chemical properties of elementary and compound substances as a progressively changing and periodically recurring function of the atomic weights.

6. **Values of the Atomic Weights.** — The existing data and all newly determined data relating to atomic weights are critically considered at frequent intervals by an International Committee on Atomic Weights, and a table is published each year showing the most probable values. The following table contains the latest values adopted for the more important elements. The values are given to such a number of decimal places that the last one is probably in error by not more than one or two units.

VALUES OF THE ATOMIC WEIGHTS

Aluminum . . . . .	Al	27.0	Lead . . . . .	Pb	207.20
Antimony . . . . .	Sb	120.2	Lithium . . . . .	Li	6.94
Argon . . . . .	A	39.9	Magnesium . . . . .	Mg	24.32
Arsenic . . . . .	As	74.96	Manganese . . . . .	Mn	54.93
Barium . . . . .	Ba	137.37	Mercury . . . . .	Hg	200.6
Beryllium . . . . .	Be	9.1	Neon . . . . .	Ne	20.2
Bismuth . . . . .	Bi	209.0	Nickel . . . . .	Ni	58.68
Boron . . . . .	B	10.9	Nitrogen . . . . .	N	14.008
Bromine . . . . .	Br	79.92	Oxygen . . . . .	O	16.00
Cadmium . . . . .	Cd	112.40	Phosphorus . . . . .	P	31.04
Calcium . . . . .	Ca	40.07	Platinum . . . . .	Pt	195.2
Carbon . . . . .	C	12.005	Potassium . . . . .	K	39.10
Chlorine . . . . .	Cl	35.46	Radium . . . . .	Ra	226.0
Chromium . . . . .	Cr	52.0	Silicon . . . . .	Si	28.1
Cobalt . . . . .	Co	58.97	Silver . . . . .	Ag	107.88
Copper . . . . .	Cu	63.57	Sodium . . . . .	Na	23.00
Fluorine . . . . .	F	19.0	Strontium . . . . .	Sr	87.63
Gold . . . . .	Au	197.2	Sulfur . . . . .	S	32.06
Helium . . . . .	He	4.00	Thallium . . . . .	Tl	204.0
Hydrogen . . . . .	H	1.008	Tin . . . . .	Sn	118.7
Iodine . . . . .	I	126.92	Titanium . . . . .	Ti	48.1
Iron . . . . .	Fe	55.84	Zinc . . . . .	Zn	65.37

## 7. Chemical Formulas, Formula-Weights, and Equivalent-Weights. —

In order to express the gravimetric composition of compounds, the symbols of the elements are considered to represent their atomic weights and are written in sequence with such integers as subscripts as will make the resulting formula express the proportions by weight of the elements in the compound.

The formula is commonly so written as to represent also the number of atoms of each element present in the molecule.

The formula represents, in addition, a definite weight of the substance, namely the weight in grams which is equal to the sum of the numbers represented by the symbols of the elements in the formulas. This weight is called the *formula-weight* of the substance. Thus the formula  $\text{HNO}_3$  denotes  $1.008 + 14.01 + (3 \times 16.00)$  or 63.02 grams of nitric acid.

Those weights of various substances which enter into chemical reactions with one another are called *equivalent-weights*. Adopting one formula-weight or 1.008 grams of the element hydrogen as the standard of reference, the *equivalent-weight* or *one equivalent* of any substance is defined to be that weight of it which reacts with this standard weight of hydrogen, or with that weight of any other substance which itself reacts with this standard weight of hydrogen. Thus the equivalent-weight of each of the following substances is that fraction of its formula-weight which is indicated by the coefficient preceding the formula:  $\frac{1}{2}\text{Cl}_2$ ;  $\frac{1}{4}\text{O}_2$ ;  $1\text{Ag}$ ;  $\frac{1}{2}\text{Zn}$ ;  $\frac{1}{3}\text{Bi}$ ;  $1\text{NaOH}$ ;  $\frac{1}{2}\text{Ba(OH)}_2$ ;  $\frac{1}{2}\text{H}_2\text{SO}_4$ ;  $\frac{1}{3}\text{H}_3\text{PO}_4$ ;  $\frac{1}{3}\text{AlCl}_3$ ;  $\frac{1}{4}\text{K}_4\text{Fe(CN)}_6$ . The equivalent-weight of a substance may have different values depending on whether it is considered with reference to a reaction of metathesis or to one of oxidation and reduction. Thus, the metathetical equivalent of ferric chloride is  $\frac{1}{3}\text{FeCl}_3$ , but its oxidation-equivalent (with respect to its conversion to ferrous chloride) is  $1\text{FeCl}_3$ ; the metathetical equivalent of potassium chlorate is  $1\text{KClO}_3$ , but its oxidation-equivalent (with reference to its reduction to  $\text{KCl}$ ) is  $\frac{1}{6}\text{KClO}_3$ .

## CHAPTER II

### THE MOLAL PROPERTIES OF GASES AND THE MOLECULAR AND KINETIC THEORIES

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#### I. THE VOLUME OF GASES IN RELATION TO PRESSURE, TEMPERATURE, AND MOLAL COMPOSITION

**8. The Volume of Perfect Gases in Relation to Pressure and Temperature.** — Properties whose magnitudes are determined primarily by the number, and not by the nature, of the molecules present are called *molal properties*. The properties of this kind exhibited by gases are considered in this chapter.

The properties of gases, in general, conform more and more closely to certain limiting laws, known as the *laws of perfect gases*, as their pressure approaches zero. The principles relating to the effects of pressure and temperature on the volume of perfect gases will be first considered.

At any definite temperature the pressure  $p$  of a definite weight  $m$  of any perfect gas is inversely proportional to its volume  $v$ ; or its pressure-volume product  $p v$  is independent of its pressure or volume. Since *density* ( $d$ ) is defined to be the ratio ( $m/v$ ) of the weight of a substance to its volume, this law may also be stated as follows: At any definite temperature the density of any definite perfect gas is proportional to its pressure. This principle is known as *Boyle's law*.

The pressure-volume product increases with rise in temperature by the same fractional amount for different perfect gases when they are heated from the same initial to the same final temperature. For example, the pressure-volume product increases by 36.612 percent of its value at  $0^\circ$  when the temperature becomes  $100^\circ$ , whatever be the nature of the perfect gas. This law is known as the *law of temperature-effect*. It is mathematically expressed by the equation  $(p_2 v_2 - p_1 v_1)/(p_1 v_1) = f(t_1, t_2)$ , where  $f(t_1, t_2)$  denotes the same function of the temperatures  $t_1$  and  $t_2$  whatever be the nature of the perfect gas.

The form of the functional relation between the pressure-volume product and the temperature evidently depends on the definition of temperature adopted; and this relation assumes the simplest form when the concept of absolute temperature is employed. For absolute

temperature is so defined that it is directly proportional to the pressure-volume product of a perfect gas; that is, it is defined by the equation  $T/T_0 = (pv)/(p_0v_0)$ , where  $p_0v_0$  is the value of  $p v$  at any specified temperature  $T_0$ , which for definiteness may here be taken as that of ice when melting under a pressure of one atmosphere. The value of  $T_0$  is dependent on the temperature-scale adopted. We may determine its value on the centigrade scale from the following considerations. This scale is based on the convention that there shall be a difference of 100 degrees between the temperature of melting ice and the temperature of boiling water, when both are at a pressure of one atmosphere. Now by writing the preceding equation in the form  $(T - T_0)/T_0 = (pv - p_0v_0)/p_0v_0$ , and substituting for  $T - T_0$  the value 100 and for the second member the quantity 0.36612 given in the preceding paragraph, we find the value  $273.14^\circ$  for  $T_0$ , the temperature of melting ice at a pressure of 1 atm. on the absolute centigrade scale. Since this temperature is called  $0^\circ$  on the ordinary centigrade scale, and since this scale, like the absolute scale, is based on the convention of proportionality between increase of temperature and the increase in the pressure-volume product of a perfect gas, the absolute centigrade temperature  $T$  is always equal to the ordinary centigrade temperature  $t$  increased by 273.14, or approximately **273**; black-face type being used here and throughout the book to show approximate values, given with an accuracy of 0.1 — 0.2 percent, of fundamental constants which it is well to remember.

The laws above stated, the definition of absolute temperature, and the obvious proportionality between the value of the pressure-volume product and the weight  $m$  of the gas are all expressed by the equation  $p v = m \bar{R} T$ , in which  $\bar{R}$  is a constant, evidently representing the value of  $p v/T$  for one gram of the gas, which has different values for different gases.

*Prob 1. — Derivation from Experimental Data of  $p v/T$  for One Gram of Carbon Dioxide.* — *a.* From the fact that the density of carbon dioxide is 0.0019765 g. per ccm. at  $0^\circ$  and 1 atm., calculate the exact value of  $p v/T$  under these conditions for one gram of the gas. *b.* Taking into account the fact that at this temperature and pressure the density has been found, by extrapolating from a series of measurements made at pressures between 0.1 and 1 atm., to be 0.68% greater than that required by the perfect-gas law, calculate for this gas the value of the constant  $\bar{R}$ , the pressure being expressed in atmospheres and the volume in cubic centimeters. *Ans. b, 1.8649.*

### 9. Law of Combining Volumes and the Principle of Avogadro. —

The foregoing physical laws acquire an important chemical significance by reason of the *law of combining volumes*, which may be stated as follows: Those quantities of perfect gases that are involved in chemical reactions with one another have, at the same temperature and pressure volumes, which are equal or small multiples of one another. Thus the quantities of hydrogen and of oxygen which unite with each other to form water have volumes whose ratio approaches the exact value 2:1 as the pressure of the gases approaches zero. In other words, those quantities of different substances which as perfect gases have the same value of the product  $p v/T$  are equal to, or are small multiples of, the quantities which are involved in chemical reactions with one another. Now, since according to the molecular theory substances react by molecules, these quantities of different perfect gases which have the same value of  $p v/T$  must contain either an equal number of molecules or small multiples of an equal number.

These considerations suggest a simpler principle, known as the *principle of Avogadro*, which may be stated as follows: Those quantities of different perfect gases which have the same volume at the same temperature and pressure, and therefore the same value of  $p v/T$  at any temperature and pressure, contain an *equal* number of molecules. The densities of different perfect gases at the same temperature and pressure are therefore proportional to the weights of their molecules.

This principle, originally hypothetical, has now been so fully verified that it has become one of the fundamental laws of chemistry.

**10. Empirical Definition of Molecular Weight and of Mol. —** The principle of Avogadro evidently enables the relative weights of the molecules of different gaseous substances to be determined. To express these relative weights more definitely, the ratio of the weight of the molecule of any substance to the weight of the molecule of oxygen taken as 32 is commonly considered, this ratio being called the *molecular weight*  $M$  of the substance. The number 32 is adopted as the reference quantity of oxygen, since (as shown in Prob. 15) it corresponds to the adoption of 16 as the atomic weight of oxygen.

The so-defined molecular weight of a substance may evidently be experimentally determined by finding the number of grams of it which have that value of  $p v/T$  which 32 grams of oxygen have, when both substances are in the state of perfect gases. This number of grams is called *one mol* or *one molal weight* of the substance.

The mol is a unit of great importance in chemical considerations, both because it is directly related to molecular weight and because it makes possible a general expression of the laws of perfect gases.

**11. General Expression of the Laws of Perfect Gases.** — Representing by  $R$  the constant value of  $p v/T$  for one mol and by  $N$  the number of mols of the gas present, the laws of perfect gases may be expressed in a general form by the following equation, hereafter called the *perfect-gas equation*:

$$p v = NRT.$$

The numerical value of the *gas-constant*  $R$  depends on the units in which the pressure, volume, and temperature are expressed. In scientific work, temperature is always expressed in centigrade degrees (here on the absolute scale); volume is ordinarily expressed in cubic centimeters or liters; and pressure in dynes per square centimeter, millimeters of mercury, or atmospheres. One *dynes* is a force of such magnitude that when it acts on a freely moving mass of one gram it increases its velocity each second by one centimeter per second; and the pressure of one dyne per square centimeter is called one *bar*,  $10^6$  bars being called one *megabar*. One *atmosphere* is a pressure equal to that exerted by a column of mercury 76 cm. in height at  $0^\circ$  at the sea-level in a latitude of  $45^\circ$ . The value of the gas-constant  $R$  when the pressure is in atmospheres and the volume is in cubic centimeters is 82.07 (approximately 82). Its value when the pressure is in dynes per square centimeter and the volume is in cubic centimeters is  $8.316 \times 10^7$  ergs per degree. Its value will later be shown to be 1.985 calories per degree.

*Prob. 2. — Value of the Atmosphere.* — Calculate the value of the atmosphere in dynes per sqcm. and in megabars. The density of mercury at  $0^\circ$  is 13.60. The force of gravity acting on any freely moving body increases its velocity each second by  $g$  centimeters per second. The value of  $g$  at the sea-level in a latitude of  $45^\circ$  is 980.6 (980) centimeters per second. *Ans.*  $1.013 \times 10^6$  dynes per sqcm.

*Prob. 3. — Calculation of the Gas-Constant.* — *a.* Calculate precisely the value of the gas-constant  $R$  when the pressure is in atmospheres and the volume in cubic centimeters, from the fact that one gram of oxygen has a volume of 7005 ccm. at  $0^\circ$  and 0.1 atm., under which conditions oxygen does not deviate appreciably from the perfect-gas law. *b.* Calculate also the value of  $R$  when the pressure is in dynes per square centimeter, and the volume is in cubic centimeters. *c.* Calculate the volume of one mol of a perfect gas at  $20^\circ$  and 1 atm. *Ans. c,* 24060 ccm. (approximately 24 l.)

*Applications of the Perfect-Gas Laws. —*

*Note.* — In the following problems, and in general throughout the book, assume, unless otherwise indicated, as an approximation sufficient for many purposes, that gases at pressures not exceeding 1 atm. conform to the perfect-gas equation.

X *Prob. 4.* — Seven grams of a certain gas have a volume of 6.35 l. at 20° and 720 mm. How many grams make one mol?

X *Prob. 5.* — *a.* What is the volume occupied by 12 g. of ether vapor ( $C_4H_{10}O$ ) at 80° and 600 mm.? *b.* What is the density? *c.* What is the ratio of the density to that of oxygen at the same temperature and pressure?

X *Prob. 6.* — How many grams of iron must be taken to produce by its action on sulfuric acid one liter of hydrogen ( $H_2$ ) at 27° and 1 atm.?

It will be seen in Art. 12 that, though air is a mixture, it has in different localities a fairly constant composition and that the pressures of its separate constituents are determined by the perfect-gas laws. The pressure of the air as a whole, and its pressure-volume-temperature relations in general, can therefore be simply computed with the aid of the perfect-gas equation by regarding air as a single substance having a molal weight equal to the number of grams of air which have the same value of  $p v/T$  as 32 grams of oxygen. The so-defined molal weight of air is computed from the most accurate density determinations to be 28.98 (approximately 29).

*Prob. 7.* — *Calculation of the Molal Weight of Air.* — Calculate the molal weight of pure dry air from the fact that its density is 0.0012930 at 0° under a pressure of 760 mm. of mercury at sea-level in latitude 45°.

**12. Dalton's Law of Partial Pressures.** — The (total) pressure  $p$  of a mixture of substances in the gaseous state is evidently the sum of the pressures  $p_1, p_2 \dots$  of the separate substances. That is,  $p = p_1 + p_2 + \dots$ . The pressures of the separate substances are called the *partial pressures*.

Partial pressures in the case of perfect gases may be calculated as described below. They cannot be directly measured, except in cases where a *semipermeable wall*, that is, a wall permeable for only one of the substances present in the gas mixture, can be found. Thus, when a platinum vessel containing a mixture of hydrogen and nitrogen at a high temperature is immersed in an atmosphere of hydrogen, hydrogen passes through the platinum walls until its pressures within and without the vessel become equal; the difference then observed between the total pressure of the mixture within the vessel and the pressure of the hydrogen outside is due to the nitrogen, which does not pass through the wall; and this difference is equal to its partial pressure.

The pressure of a mixture of substances in the state of a perfect gas is found to be equal to the sum of the partial pressures calculated by the principle that each chemical substance (defined as in Art. 4 to be a substance consisting of molecules of one particular kind) has the same pressure as it would if it were alone present in the volume occupied by the mixture. This principle, which is of great importance in chemical considerations, is known as *Dalton's law of partial pressures*.

In accordance with this law and the perfect-gas law, the partial pressures of the separate substances are evidently given by the expressions,  $p_1 = N_1RT/v$ ,  $p_2 = N_2RT/v$ , ... where  $N_1, N_2, \dots$  represent the number of mols of the respective substances; and the partial pressure of any of the substances is evidently equal to the total pressure of the gas multiplied by the ratio of the number of mols of that substance to the total number of mols in the mixture. This ratio is commonly called the *mol-fraction* ( $x$ ) of that substance. That is,  $p_1 = p x_1$ , where  $x_1 = N_1/(N_1 + N_2 + \dots)$ .

Air affords an important example of these considerations. Pure dry air has at different times and places a fairly constant composition; namely, it contains approximately 21.0 mol-percent of oxygen ( $O_2$ ), 78.0 mol-percent of nitrogen ( $N_2$ ), 0.94 mol-percent of argon (A), and 0.03 mol-percent of carbon dioxide ( $CO_2$ ), and, in accordance with Dalton's law, the partial pressures of these four substances in air are 21.0, 78.0, 0.94, and 0.03 percent, respectively, of the total pressure of the air. As will be shown later, it is these partial pressures, not the total pressure of the air, which determine the quantities of the respective substances which dissolve in water when it is shaken with air, and it is the partial pressure of the oxygen which determines the equilibria of oxidation reactions taking place in air.

#### *Applications of the Law of Partial Pressures. —*

*Prob. 8.* — A Bessemer converter is charged with 10000 kg. of iron containing 3% of carbon. *a.* How many cubic meters of air at  $27^\circ$  and 1 atm. are needed for the combustion of all the carbon, assuming one third to burn to  $CO_2$  and two thirds to  $CO$ ? *b.* What are the partial pressures of the gases evolved? *Ans. a,* 1950 cubic meters.

*Prob. 9.* — In making sulfur dioxide for use in the contact process of manufacturing sulfur trioxide, 30 kg. of sulfur are charged into each burner per hour, and such an excess of air is introduced (to insure complete combustion) as to produce a gas mixture containing 10 mol-percent of oxygen. How many cubic meters of air at  $20^\circ$  and 1 atm. must be introduced per hour? *Ans.* 205 cubic meters.

*Determination of the Dissociation of Gases by Density Measurements.* —

*Prob. 10.* — A certain fraction  $\gamma$  (or a certain percentage  $100\gamma$ ) of gaseous nitrogen tetroxide is dissociated according to the reaction  $\text{N}_2\text{O}_4 = 2\text{NO}_2$  at any definite pressure  $p$  and temperature  $T$ . *a.* Find an expression for the total number of mols  $i$  (of  $\text{N}_2\text{O}_4$  and  $\text{NO}_2$ ) that result under these conditions from one formula-weight  $M$  (92 g.) of nitrogen tetroxide taken. *b.* Find an expression for the volume  $v$  that would be occupied by one formula-weight of the nitrogen tetroxide at the pressure  $p$  and temperature  $T$ . *c.* Find a corresponding expression for the density  $d$  of the vapor. *Ans.*  $d = Mp/(iRT)$ .

*Prob. 11.* — Calculate the dissociation of nitrogen tetroxide at  $50^\circ$  and 500 mm. from the following data: a balloon filled with it at this temperature and pressure weighs 71.981 g.; the same balloon when evacuated weighs 71.217 g., and when filled at  $25^\circ$  with water (whose density at  $25^\circ$  is 0.997) weighs 555.9 g. *Ans.* 45%.

**13. Determination of Molecular Weights.** — The experimental determination of the molecular weight of a gaseous substance consists in measuring the volume of a weighed quantity of the substance at an observed pressure and temperature. From these quantities ( $v$ ,  $m$ ,  $p$ , and  $T$ ) the molecular weight of the substance is calculated with the aid of the perfect-gas equation.

*Prob. 12.* — *Experimental Determination of Vapor-Density by Hofmann's Method.* — 0.1035 g. of a volatile liquid is introduced into the vacuum above a mercury column in a graduated tube standing in an open vessel of mercury. The tube is entirely surrounded by a jacket through which steam at  $100^\circ$  is passed. The mercury column falls till it stands 260 mm. above the mercury-level in the vessel below, and the volume of the completely vaporized liquid is observed to be 63.0 ccm. The barometric pressure at the time is 752 mm. At  $100^\circ$  the density of mercury is 13.35, and its vapor-pressure is negligible. Make a sketch showing the apparatus; and calculate the density and molecular weight of the vapor. *Ans.*  $d = 0.001645$ ;  $M = 76.8$ .

*Prob. 13.* — *Experimental Determination of Molecular Weight by the Air-Displacement Method of Victor Meyer.* — A cylindrical bulb provided with a long stem is filled with dry air; and it is heated, while still open to the atmosphere, to a constant temperature (of about  $218^\circ$ ) within a jacket filled with vapor of boiling naphthalene. The stem, which protrudes above the vapor jacket, has a side-arm which delivers into a graduated tube filled with water and inverted over water, so that the air to be later expelled from the bulb can be collected and measured. A tiny glass bottle containing 0.2210 g. of a volatile liquid substance is dropped into the heated bulb, and at the same moment the bulb is cut off from communication with the atmosphere by closing the top of the stem. The liquid rapidly vaporizes and drives out of the bulb a volume of air equal to the volume occupied by the vapor

of the substance, the pressure being always that of the atmosphere. This air collected in the measuring apparatus is found to have a volume of 24.65 ccm. at  $22^{\circ}$  under the barometric pressure of 752 mm.; but of this pressure 20 mm. is due to the pressure of water vapor. Make a sketch showing the apparatus; and calculate, *a*, the number of mols of air expelled, and *b*, the molecular weight of the vaporized substance.  
*Ans. a*, 0.000989; *b*, 225.

Since gases at atmospheric pressure conform to the perfect-gas laws only approximately, and since gaseous densities are not commonly determined with so great accuracy as the composition of substances, the exact value of the molecular weight of a compound is usually derived from the gravimetric composition, the density being employed only to determine what multiple or submultiple of the value so derived is in accordance with Avogadro's principle.

*Prob. 14. — Exact Evaluation of Molecular Weights. — a.* A certain oxide contains exactly 72.73% of oxygen. What does this show in regard to its molecular weight? *b.* At  $0^{\circ}$  and 1 atm., one liter of this (gaseous) oxide is found to weigh exactly 1.977 g. What is the molecular weight of the oxide corresponding to this datum? *c.* What is the exact molecular weight derived by considering the data relating both to the composition and density? *d.* What do these two values of the molecular weight show as to the percentage deviation of the density from that which is required by the perfect-gas equation?  
*Ans. d*, 0.68%.

**14. Derivation of the Atomic Weights of Elements and of the Molecular Composition of Compounds.** — The exact values of atomic weights are based on analytical determinations of the combining weights, as described in Art. 5. The multiple of the combining weight adopted as the *atomic weight* of any element is derived by finding the smallest weight of the element contained in one molecular weight of any of its gaseous compounds. This is the true atomic weight only in case some one of the compounds studied contains in its molecule a single atom of the element; and the adopted atomic weight is therefore strictly only a maximum value, of which the true atomic weight may be a submultiple. The probability that the true atomic weight has been found evidently increases with the number of the gaseous compounds whose molecular weights have been determined.

The multiples of the combining weights adopted as the atomic weights have, however, not been derived solely from molecular-weight determinations. From the laws relating to certain other properties, mentioned in Art. 5, independent values of the atomic weights have

been obtained, which confirm and extend those derived from molecular weights.

The *molecular composition* of a gaseous substance (that is, the number and nature of the atoms in its molecule) can evidently be derived from its molecular weight, its composition by weight, and the atomic weights of the elements contained in it. The chemical formulas of substances whose molecular weights in the gaseous state are known are ordinarily so written as to express this molecular composition. Such formulas are called *molecular formulas*.

*Derivation of Atomic Weights and Molecular Formulas.* —

*Prob. 15.* — Certain compounds have molecular weights  $M$  (referred to that of oxygen as 32) and percentages of oxygen  $x$  as follows: Sulfur trioxide,  $M = 80.07$ ,  $x = 59.95$ ; water,  $M = 18.02$ ,  $x = 88.80$ ; carbon dioxide,  $M = 44.00$ ,  $x = 72.73$ . *a.* Find the weight of oxygen contained in one molecular weight of each of these oxides. *b.* What conclusion as to the atomic weight of the element oxygen can be drawn from these results (which are based on the convention that the molecular weight of oxygen gas is 32)? *c.* What does this show as to the number of atoms in the molecule of oxygen gas?

*Prob. 16.* — *a.* Calculate the combining weight of the element contained in the oxide whose composition was given in Prob. 14*a*. *b.* What conclusion as to its atomic weight can be drawn from this combining weight and the density given in Prob. 14*b*? *c.* What conclusion can be drawn as to the molecular formula of the oxide?

*Prob. 17.* — *a.* The chloride of a certain element is found by analysis to contain 52.50% of chlorine, whose atomic weight is 35.46; and it is found to have at 150° a vapor-density 4.71 as great as that of air at the same temperature and pressure. What conclusion can be drawn from these facts as to the exact atomic weight of the element? *b.* The hydride of the same element is a gas which contains 5.91% of hydrogen; and it is found to be produced without change in volume when hydrogen ( $H_2$ ), whose atomic weight is 1.008, is passed over the solid elementary substance. What conclusion can now be drawn as to the atomic weight of the element? *c.* What are the simplest molecular formulas of the hydride and of the chloride consistent with these conclusions?

*Prob. 18.* — A certain hydrocarbon is composed of 92.25% of carbon and 7.75% of hydrogen, whose atomic weights are 12.00 and 1.008, respectively. Its density when in the form of vapor at 100° and 1 atm. is 2.47 times as great as that of oxygen under the same conditions. Calculate its exact molecular weight, and derive its molecular formula.

The molecules of elementary substances may consist of single atoms or of two or more atoms. Thus the molecular formulas of some of those whose density in the gaseous state has been determined are:  $H_2$ ,  $N_2$ ,  $O_2$ ,  $F_2$ ,  $Cl_2$ ,  $Br_2$ ,  $I_2$ ,  $P_4$ ,  $As_4$ ,  $He$ ,  $Ne$ ,  $A$ ,  $Hg$ ,  $Cd$ ,  $Zn$ ,  $Na$ ,  $K$ .

At very high temperatures some of these have been shown to dissociate into simpler molecules; thus above  $1500^{\circ}$  the molecule of iodine consists of a single atom.

A knowledge of the molecular formulas of substances is of importance principally because the chemical relationships of different substances are far more clearly brought out by such formulas than by the simpler ones expressing merely composition by weight. The structure theory, which underlies the science of organic chemistry, is based upon a knowledge of the molecular weights of substances.

**15. Deviations from the Perfect-Gas Laws at Moderate Pressures.** — The deviations from the perfect-gas law, so long as they do not exceed a few percent, are almost exactly proportional to the pressure. This fact is expressed by the following equation, which will be called the *gas equation at moderate pressures*:

$$pv = NRT(1 + \alpha p).$$

In this equation the coefficient  $\alpha$  evidently represents the fractional deviation at unit-pressure of the actual value of  $pv$  from that required by the perfect-gas law. The value of  $\alpha$  varies with the nature of the gas, and for a given gas with the temperature.

The following table shows the values of the percentage deviation (100  $\alpha$ ) of  $pv$  from  $NRT$  at one atmosphere for various gases at  $0^{\circ}$ , together with their condensation-temperatures at one atmosphere.

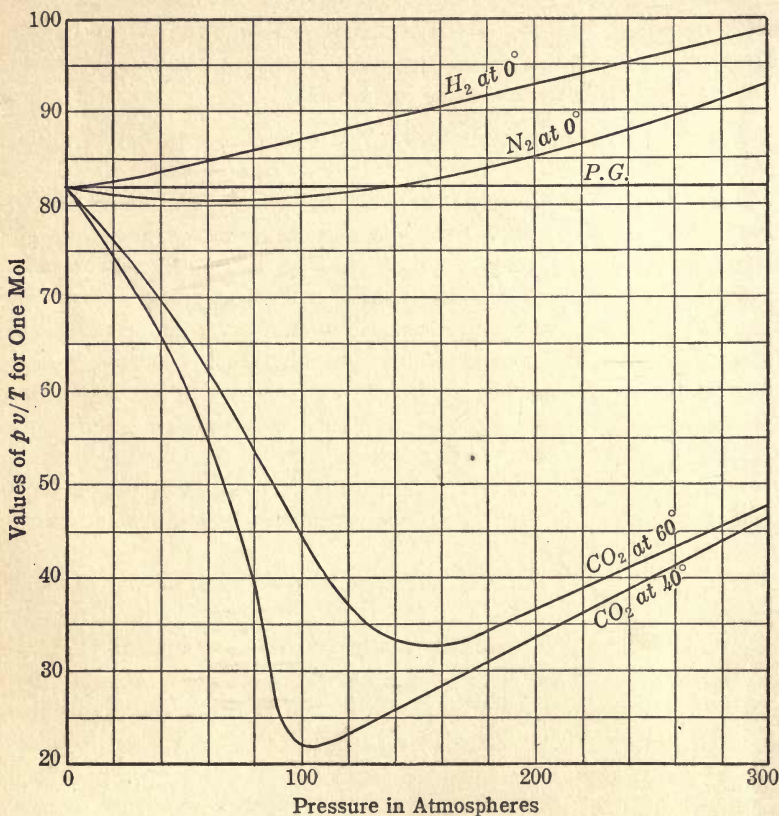
DEVIATIONS AT MODERATE PRESSURES

Formula of gas	He	H <sub>2</sub>	N <sub>2</sub>	NO	CO <sub>2</sub>	NH <sub>3</sub>	SO <sub>2</sub>
Percentage deviation	+0.06	+0.05	-0.04	-0.12	-0.68	-1.52	-2.38
Condensation-temp.	-269°	-253°	-196°	-151°	-78°	-34°	-10°

*Prob. 19. — Calculation of the Deviation-Coefficient.* — *a.* Calculate the value of the deviation coefficient  $\alpha$  for nitrous oxide (N<sub>2</sub>O) at  $0^{\circ}$  from the fact that its density at  $0^{\circ}$  and 1 atm. is 0.001978 g. per ccm. *b.* State what percentage error would be made in calculating by the perfect-gas equation the volume of this gas at  $0^{\circ}$  and 3 atm. *Ans. a.* -0.0073.

**16. Pressure-Volume Relations of Gases at High Pressures.** — In the figure are plotted the values of  $pv/T$  in atmospheres and cubic centimeters as ordinates against the values of the pressure in atmospheres as abscissas for one mol of hydrogen at  $0^{\circ}$ , of nitrogen at  $0^{\circ}$ , of carbon dioxide at  $60^{\circ}$  and at  $40^{\circ}$ , and of a perfect gas (marked P. G. in the figure). At temperatures between  $0^{\circ}$  and  $60^{\circ}$ , helium (He) and neon (Ne) have curves similar to that of hydrogen (H<sub>2</sub>); oxygen (O<sub>2</sub>), carbon monoxide (CO), and nitric oxide (NO) have curves similar

to that of nitrogen; and nitrous oxide ( $\text{N}_2\text{O}$ ), ammonia ( $\text{NH}_3$ ), and ethylene ( $\text{C}_2\text{H}_4$ ) have curves similar to those of carbon dioxide ( $\text{CO}_2$ ).



*Pressure-Volume Relations of Gases at High Pressures. —*

*Prob. 20.* — Estimate with the aid of the figure the percentage amount by which at 60 atm. the volume of  $\text{H}_2$  at  $0^\circ$ , of  $\text{N}_2$  at  $0^\circ$ , and of  $\text{CO}_2$  at  $40^\circ$  and at  $60^\circ$  deviates from that of a perfect gas.

*Prob. 21.* — Summarize the general conclusions in regard to the pressure-volume relations of gases that can be drawn from the curves of the figure, from the statements in the preceding text, and from the condensation-temperatures given in Art. 15.

*Prob. 22.* — Determine from the figure how many kilograms of  $\text{CO}_2$  can be charged into a 15-liter steel tank which will safely withstand a pressure,  $a$ , of 50 atm.;  $b$ , of 100 atm.;  $c$ , of 150 atm. Assume that the tank might be exposed (under a summer sun) to a temperature as high as  $40^\circ$ . *Ans.*  $a$ , 1.7;  $b$ , 9.6;  $c$ , 11.5.

The pressure-volume-temperature relations of gases are closely represented up to moderately high pressures by the following expressions, known as the *van der Waals equation*, in which  $a$  and  $b$  are constants (with respect to changes of volume, pressure, and temperature) varying with the nature of the gas:

$$\left(p + \frac{aN^2}{v^2}\right)(v - Nb) = NRT; \text{ or for one mol, } \left(p + \frac{a}{\tilde{v}^2}\right)(\tilde{v} - b) = RT.$$

With reference to the volume occurring in the second of these expressions, it may be noted that, in general, quantities referred to one mol are called *molal quantities*, and those referred to one gram *specific quantities*; and that in this book the former are designated by a wavy line, and the latter by a straight line, above the symbol of the quantity. Thus,  $\tilde{v}$  denotes the *molal volume*, the volume of one mol, and  $\bar{v}$  denotes the *specific volume*, the volume of one gram, of substance. The term *specific* is also applied to quantities which are referred to unit-values of other determining factors such as the volume, length, or cross-section; thus specific resistance denotes the electrical resistance of a mass of the substance one centimeter long and one square centimeter in cross-section.

The applicability of this equation and its theoretical significance are discussed in Art. 20.

Any equation which, like the van der Waals equation, the perfect-gas equation, or the gas equation at moderate pressures, expresses the relation between the volume, pressure, and temperature of a substance within a certain range of conditions is called the *equation of state* of the substance under those conditions.

## II. THE KINETIC THEORY

**17. The Fundamental Kinetic Hypotheses.** — The molecular theory has, with the aid of certain hypotheses in regard to the motion of molecules, been developed into a body of principles, collectively known as the *kinetic theory*. ✓ The two most fundamental of these hypotheses, which express from a molecular viewpoint the nature of pressure and of temperature, respectively, are as follows:

The molecules of gaseous or liquid substances are continually in motion in all directions, the motions taking place in accordance with the ordinary laws of mechanics. The molecules are constantly colliding with one another and with the walls of the containing vessel; but no loss of kinetic energy results from these collisions. The pressure of the substance on the walls is the integrated effect of the impacts of its molecules. This may be called the *kinetic pressure hypothesis*.

At the same temperature the molecules of different fluid (that is, gaseous or liquid) substances have the same kinetic energies, whatever be the masses of their molecules or the pressure or volume of the substance; that is, for two different substances at the same temperature,  $\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2$ , where  $m_1$  and  $m_2$  represent the masses of the two kinds of molecules, and  $u_1$  and  $u_2$  their velocities. The kinetic energy of the molecules increases with the temperature, and it is determined solely by it. Mathematically expressed,  $\frac{1}{2}m u^2 = f(T)$ , where  $f(T)$  is a function which is identical for all fluid substances. This may be called the *kinetic temperature hypothesis*.

**18. The Kinetic Equation for Perfect Gases.** — From the kinetic pressure hypothesis may readily be derived an expression in terms of the molecular quantities for the pressure-volume product of a perfect gas, as shown in the following problem. In this derivation two simplifying assumptions, admissible in the case of a perfect gas, are made; namely, that the volume of the molecules is negligible in comparison with the volume of the gas, and that any force of attraction between the molecules is negligible because of the relatively large mean distances between them. This expression is:

$$p v = \frac{1}{3} n m u^2.$$

In this equation  $n$  denotes the number of molecules in the volume  $v$  of the gas at the pressure  $p$ ,  $m$  the mass of a single molecule, and  $u$  the velocity of the molecules. It may be called the *kinetic equation for perfect gases*.

*Prob. 23. — Derivation of the Kinetic Equation.* — A volume  $v$  of a perfect gas is contained in a cubical vessel whose edges have the length  $l$ . The gas consists of  $n$  molecules, each of mass  $m$ . Consider that all the molecules are moving with the same velocity,  $u$ , and that the motions of these molecules, which in reality take place in all directions, are resolved in the three directions perpendicular to the faces of the cube, which is equivalent to assuming that one third of all the molecules is moving in each of these directions. *a.* Find the number of impacts which any one molecule makes on the opposite faces in a unit of time. *b.* Find the total number of impacts which all the molecules make on all the faces in a unit of time. *c.* Show that the number of impacts which the molecules make on a unit of surface in a unit of time is  $\frac{1}{3}nu/v$ . *d.* Find the change of momentum which attends each impact, taking account of the fact that the molecule rebounds from the wall with a velocity equal to that with which it strikes it. *e.* Find the change of momentum of all the molecules that strike a unit of surface in a unit of time. *f.* Noting that this, in accordance with the general equation of mechanics  $f = m(du/dt)$ , is equal to the force ( $f$ ) exerted on the unit of surface or to the pressure, show that the pressure-volume product is expressed by the equation  $p v = \frac{1}{3} n m u^2$ .

The derivation given in the preceding problem is not conclusive, since it involves an assumption as to the directions of motion of the molecules; but a rigorous analysis leads to the same kinetic equation. It is important to note, however, on account of its bearing on certain surface phenomena, that the rigorous treatment, which takes into account the fact that molecules approach the surface not only normally but obliquely in all directions, leads to the conclusion that the actual number of impacts made by all the molecules on unit-surface in unit-time is larger than that derived above; this actual number being given by the expression  $0.23 n u/v$ , instead of by  $\frac{1}{3} n u/v$ .

From the kinetic equation Boyle's law may be immediately deduced. For, since a change only in the volume of the gas will not cause a variation in the number of molecules  $n$  (unless they are thereby caused to associate or dissociate), and since the kinetic energies  $\frac{1}{2} m u^2$  of the separate molecules will remain constant, in accordance with the kinetic temperature hypothesis, so long as the temperature remains unchanged, it follows that also the product  $p v$  will undergo no change when the volume is varied at a constant temperature.

The law of temperature-effect is also a consequence of the kinetic equation; for any definite change in temperature must evidently cause the same change in the pressure-volume product of different gases, since it causes the same change in the kinetic energy of their molecules.

The principle of Avogadro also is readily derived from the kinetic equation for perfect gases and from the kinetic temperature hypothesis. Thus, for two perfect gases with equal pressure-volume products,  $p_1v_1 = p_2v_2$ , and therefore  $\frac{1}{3}n_1m_1u_1^2 = \frac{1}{3}n_2m_2u_2^2$ ; and for the case that they have also equal temperatures,  $\frac{1}{2}m_1u_1^2 = \frac{1}{2}m_2u_2^2$ ; whence follows  $n_1 = n_2$ . That is, those quantities of different perfect gases which at any definite temperature have equal pressure-volume products consist of an equal number of molecules.

Certain principles relating to the velocity of the molecules, and even the exact absolute values of their velocities, can be derived from the kinetic equation in the ways illustrated by the following problems.

*Velocity of the Molecules. —*

*Prob. 24. — a.* Show how the velocities of the molecules of different gases at the same temperature are related to the molecular weights of the gases; illustrating by hydrogen and oxygen. *b.* Show how the velocities of the molecules of the same gas at different temperatures are related to those temperatures; illustrating by oxygen at  $0^\circ$  and  $100^\circ$ .

*Prob. 25. —* Calculate the velocity of the molecules of oxygen at  $20^\circ$  in kilometers and in miles per second. *Ans.* 0.478 km.; 0.30 mile.

**19. The Kinetic Energy of the Molecules and the Avogadro Number. —** An expression may be readily derived for the kinetic energy  $K$  due to the translatory motion of the  $n$  molecules present in any mass of a perfect gas. Namely, for this kinetic energy, which is obviously equal to  $\frac{1}{2}nm u^2$ , the following expression is obtained at once by combining the kinetic equation for perfect gases,  $pv = \frac{1}{3}nm u^2$ , with the perfect-gas equation,  $pv = NRT$ :

$$K = \frac{1}{2} n m u^2 = \frac{3}{2} NRT.$$

From this equation the increase  $dK/dT$  of the kinetic energy of the molecules in one mol of gas per degree of temperature is seen to be  $\frac{3}{2}R$ , which is readily shown to have the value 12.474 ergs or 2.978 (approximately 2.98) calories.

*Prob. 26. — Kinetic Energy of the Molecules. — a.* Calculate the translatory kinetic energy in ergs and calories of the molecules in one mol of a perfect gas at  $20^\circ$ . *b.* Show that the increase in this kinetic energy per degree is 2.98 cal. Note that 1 cal. equals  $4.182 \times 10^7$  ergs.

The corresponding expression for the kinetic energy of a single molecule evidently is:

$$\frac{1}{2} m u^2 = \frac{3}{2} \frac{RT}{n/N} = \frac{3}{2} \frac{RT}{\bar{n}}.$$

The quantity  $n/N$ , which represents the number of molecules in one mol of any substance (for example, in 2.015 grams of hydrogen or 32.00 grams of oxygen), is a fundamental constant known as the *Avogadro number* ( $\tilde{n}$ ). Its value has been recently determined by a variety of independent methods. The most probable value is  $6.06 \times 10^{23}$ .

The above derived expression for  $\frac{1}{2}mu^2$  is the general form, holding true for all fluid substances, of the functional relation between temperature and kinetic energy of the separate molecules, which is postulated in the kinetic temperature hypothesis. For, since according to that hypothesis this kinetic energy is the same function of the temperature for all fluid substances, and since it has been shown to be proportional to the absolute temperature for a perfect gas, it follows that it is proportional to the absolute temperature for all fluid substances. In other words, the mathematical expression of the kinetic temperature hypothesis, which was given in the indefinite form  $\frac{1}{2}mu^2 = f(T)$ , may now be written in the definite form  $\frac{1}{2}mu^2 = \frac{3}{2}kT$ ; where  $k$  is a constant (equal to  $R/\tilde{n}$ ) with respect to any variation whatsoever of the nature or state of the fluid substance. The value of the fundamental constant  $k$  is readily calculated from the previously given values of  $R$  and  $\tilde{n}$ , and is thus found to be  $1.372 \times 10^{-16}$  ergs per degree.

*Prob. 27. — The Number and the Mass of the Molecules. — a.* Show that the number of molecules in 1 ccm. of a perfect gas at  $20^\circ$  and 1 atm. is  $2.51 \times 10^{19}$ . *b.* Calculate the mass of one molecule of hydrogen, and that of one atom of chlorine.

**20. The Kinetic Equation for Imperfect Gases.** — As the pressure of a gas increases, the two effects that were neglected in the derivation of the kinetic equation for perfect gases (Art. 18) must be taken into account; namely, the effect of the volume occupied by the molecules themselves, and the effect of forces of attraction between the molecules. These influences affect respectively the two factors involved in the derivation of the equation — the number of impacts on the unit of surface in the unit of time, and the force corresponding to each impact. For the number of impacts made by a row of molecules moving between the opposite faces of the cube will evidently be increased when the distance which the molecules have to traverse becomes appreciably shortened by collisions between them. And the force produced by the impact of each molecule will evidently be

diminished if, as it approaches the wall, it is appreciably attracted by the molecules behind it so that it strikes the wall with a smaller momentum.

\*The correction to be applied to the kinetic equation for perfect gases for the volume of the molecules may be derived by considering the number and character of the collisions (whether head-on, glancing, or tangential) and the shortening of the path by each type of collision, and by integrating the separate effects. It is evident that the resultant effect will be dependent on the size of the molecules; and under certain simplifying assumptions it can be shown, if the volume of one molecule be represented by  $\phi$ , that the distance between the opposite faces of the cube actually traversed by the molecules is reduced in consequence of the collisions from  $l$  to  $l(v - 4n\phi)/v$ . The number of impacts by all the molecules on unit-surface in unit-time is increased in the same proportion, namely,

$$\text{from } \frac{nu}{6v} \text{ (as found in Prob. 23c) to } \frac{nu}{6(v - 4n\phi)}.$$

\*The effect of the attraction of the molecules on the momentum with which a molecule strikes the wall can be derived from the following considerations. The decrease in its momentum  $mu$  must be proportional to the force acting on it and to the time during which that force acts. The force of attraction must, however, be proportional to the number of molecules  $n/v$  in the unit of volume; and the time during which the molecule is subjected to this attraction, which is the time required for it to traverse the outer layers of the gas, must be inversely proportional to its velocity, which is  $uv/(v - 4n\phi)$ ; this velocity being greater than  $u$ , the velocity between collisions, because of the just considered effect of the volume of the molecules. The change in momentum attending the impact of the molecule on the wall will therefore be reduced

$$\text{from } 2mu \text{ to } 2\left(mu - \frac{\alpha n}{uv^2}(v - 4n\phi)\right),$$

where  $\alpha$  is a proportionality-constant dependent on the nature of the gas under consideration. The change of momentum of all the molecules striking the unit of surface in the unit of time, which is equal to

\* Articles, paragraphs, and problems to which an asterisk is prefixed may be omitted in briefer courses.

the pressure  $p$ , is found by multiplying this quantity by the quantity derived in the preceding paragraphs. The product so obtained is

$$\frac{nm u^2}{3(v-4n\phi)} - \frac{\alpha n^2}{3v^2} = p.$$

\*It is evident from this equation that the externally manifested pressure  $p$  is the resultant of an outward-directed pressure (represented by the first term of the equation) caused by the motion of the molecules, and an inward-directed pressure (represented by the second term) caused by the attraction of the molecules within the gas for those in the outer or surface layers.

By considering the corrections for the volume and attraction of the molecules there may be derived (in the way just shown) the following expression, which may be called the *kinetic equation for imperfect gases*:

$$\left(p + \frac{\alpha n^2}{3v^2}\right)(v - 4n\phi) = \frac{1}{3} n m u^2.$$

In this equation  $\phi$  denotes the volume of a single molecule of the substance, and  $\alpha$  represents a constant characteristic of the substance which expresses the effect of the attraction of its molecules.

Now, since it has been shown (in Art. 18) that for any gaseous or liquid substance  $\frac{1}{3}nm u^2 = NRT$ , and since the number of molecules  $n$  may evidently be replaced in the second and fourth terms by the number of mols  $N$  of the substance with new proportionality-constants, this expression may be transformed into the following one, known as the *van der Waals equation*, already mentioned in Art. 16:

$$\left(p + \frac{aN^2}{v^2}\right)(v - Nb) = NRT.$$

By considering one mol of the substance,  $N$  becomes equal to unity, and the equation assumes the simpler form which is often conveniently employed.

It is evident from the derivation that the quantity  $b$  in the van der Waals equation denotes four times the volume of the molecules in one mol of the gas; and that the term  $aN^2/v^2$  or  $a/\tilde{v}^2$  denotes the inward-directed pressure due to the attraction of the molecules. This pressure is called the *cohesion pressure*; and the constant  $a$  may be called the *cohesion constant*.

Since the cohesion-constant  $a$  and the volume-constant  $b$  vary with the nature of the molecule, it is evident that the van der Waals equation involves the assumption that the molecules of the substance do not undergo a change through association as the pressure increases, or through dissociation as the temperature rises. These effects are, in fact, of not infrequent occurrence; and the limits of applicability of the equation must therefore be determined experimentally for each substance.

With many substances, probably with all of those whose molecules are all of one kind, the van der Waals equation gives values of the pressure or volume which agree with the observed values within one or two percent, so long as the pressure does not much exceed 20 atmospheres, or so long as the molal volume is not less than 1000 ccm. But it may lead to very erroneous results when applied, as it sometimes is, at much higher pressures (for example, to the computation of the critical constants). At these higher pressures a satisfactory correspondence with the observed values can be attained by expressing the quantities  $a$  and  $b$  as definite functions of the molal volume, instead of regarding them as constants.

A comparison of the observed pressures with the calculated pressures given in the following table illustrates the validity of the van der Waals equation for a few simple gases at molal volumes of 2000, 1000, and 500 ccm., or at pressures between 12 and 40 atmospheres. The constants used in calculating the pressures are given in the last two columns. In evaluating them the pressure is expressed in atmospheres and the volume in cubic centimeters, and they are referred to one mol of the gas. They are so chosen as to reproduce the observed pressure-volume relations accurately at pressures up to 10 or 12 atmospheres.

VALIDITY OF THE VAN DER WAALS EQUATION

Sub- stance	Temper- ature	Molal Volume	Observed Pressure	Calculated Pressure	Constants	
					$10^{-6} a$	$b$
N <sub>2</sub>	0°	1000	22.2	22.2	1.26	47
		500	44.2	44.4		
CO <sub>2</sub>	40°	2000	12.1	12.2	6.23	128
		1000	22.8	23.2		
		500	40.6	44.1		
NH <sub>3</sub>	0°	1000	16.5	16.7	10.04	163
		500	23.1	26.4		
H <sub>2</sub> O	200°	1000	29.9	30.1	10.02	210
		500	46.8	57.8		

*\*Prob. 28. — Applications of the van der Waals Equation.* — The constants  $a$  and  $b$  in the van der Waals equation have for carbon dioxide the values  $6.23 \times 10^6$  and 128, respectively, when the pressure is expressed in atmospheres and the volume in cubic centimeters. *a.* Calculate the pressure of carbon dioxide at  $40^\circ$  when the volume of one mol of the gas is 2000 ccm.; *b.* when it is 1000 ccm. *c.* Find the ratio of these computed pressures to the actual pressures, which are 12.11 and 22.84 atm., respectively. *d.* Find the ratio of the cohesion pressures to these two external pressures. *e.* Find the ratio of the correction for the volume of the molecules to the volume of the gas for these two cases. *f.* Find the ratio of the cohesion pressure to the total pressure, and the ratio of the volume correction to the total volume, for carbon dioxide at  $0^\circ$  and 1 atm. (where the molal volume is not greatly different from 22,400 ccm., that for a perfect gas). *g.* From these ratios derive the percentage deviation of  $p_v$  from  $RT$  for carbon dioxide at  $0^\circ$  and 1 atm.; and compare the result with that given in the table in Art. 15. *Ans.* *a.* 12.16 atm.; *b.* 23.24 atm.

*\*Prob. 29. — Determination of the Constants of the van der Waals Equation.* — When one mol of  $\text{NH}_3$  has a volume of 2000 ccm. at  $30^\circ$  its pressure is 11.03 atm., and when the gas is heated at this (constant) volume to  $60^\circ$ , its pressure becomes 12.37 atm. Calculate the values in atmospheres and cubic centimeters of the constants  $a$  and  $b$  for  $\text{NH}_3$  in the van der Waals equation. *Ans.*  $a = 10.03 \times 10^6$ ;  $b = 163$ .

*\*Prob. 30. — Principles Relating to the Internal Pressures.* — *a.* From the results of the preceding problem find the values of the two oppositely directed internal pressures of which the external pressure of 11.03 atm. is the resultant, for  $\text{NH}_3$  at a molal volume of 2000 ccm. at  $30^\circ$ . *b.* Find the values of the two internal pressures at  $60^\circ$ ; and state the principles which determine the effect of temperature upon each of them when the gas is kept at constant volume. *c.* Find the value of the cohesion pressure at  $30^\circ$  when the molal volume is 20,000 ccm. *Ans.* *a.* 2.51 and 13.54 atm.; *c.* 0.0251 atm.

**21. The Characteristics of the Molecules.** — From the van der Waals volume-constant and the Avogadro number the volume and diameter of a single molecule can be readily calculated, as illustrated by Prob. 31. From the diameter of the molecule the number of its collisions per second and the mean distance traversed between successive collisions can be derived as shown in the text below.

*Prob. 31. — Determination of the Dimensions of the Molecules.* — *a.* From the values, 128 and 163 ccm., of the volume-constants for  $\text{CO}_2$  and for  $\text{NH}_3$  calculate the actual volume of the molecules in one mol of each of these gases, and in 1000 ccm. of each of the gases at  $20^\circ$  and 1 atm. *b.* Assuming the molecules are spherical, calculate with the aid of the Avogadro number the diameters of the molecules of  $\text{CO}_2$  and  $\text{NH}_3$  in centimeters.

The results of determinations of these molecular magnitudes for two substances, hydrogen and carbon dioxide, at 20° and one atmosphere are given in the following table. The number of molecules per cubic centimeter and the velocity of the molecules are for comparison also included.

## MOLECULAR MAGNITUDES

	Hydrogen	Carbon dioxide
Number of molecules per cubic centimeter . . . . .	$2.5 \times 10^{19}$	$2.5 \times 10^{19}$
Velocity in centimeters per second . . . . .	$1.9 \times 10^5$	$0.4 \times 10^5$
Diameter of the molecule in centimeters . . . . .	$2.4 \times 10^{-8}$	$3.3 \times 10^{-8}$
Collisions by any one molecule per second . . . . .	$10.2 \times 10^9$	$6.2 \times 10^9$
Mean distance between collisions in centimeters . . . . .	$17.2 \times 10^{-6}$	$6.1 \times 10^{-6}$

These figures show that at atmospheric pressure the number of collisions per second is enormous and that the distance which on the average a molecule traverses between collisions is extremely small. They show, however, that this distance is several hundred times greater than the diameter of the molecule.

\*From the diameter of the molecule, as stated above, certain other quantities characteristic of the molecular condition of gases can be derived. The most important of these are the number of collisions between the molecules per second, and the average distance traversed by a molecule between the collisions, a quantity commonly called the *mean free path*. An approximate relation between the diameter of the molecules and these quantities and a fairly close estimate of their magnitudes can be derived as illustrated by Probs. 32 and 33, with the aid of the approximate assumptions that the molecules are spherical, that any one molecule under consideration is moving with a uniform velocity equal to that required by the kinetic equation, and that the other molecules among which it is moving are stationary. The number of collisions  $C$  per second which one molecule of radius  $r$  moving with velocity  $u$  makes with the other molecules when  $n$  of these are present in volume  $v$ , and the mean free path  $l$  of the molecules, are thus found to be given by the expressions:

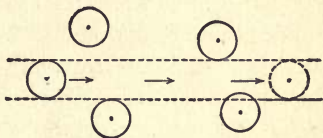
$$C = (n/v)4\pi r^2 u; \text{ and } l = \frac{1}{(n/v)4\pi r^2}.$$

\*It is seen that, as would be expected, the number of collisions per second is proportional to the number of molecules ( $n/v$ ) per unit volume, to the cross-section ( $\pi r^2$ ) of the molecules, and to their velocity ( $u$ ); and that the mean distance traversed between collisions is in-

versely proportional to the number of molecules and to their cross-section. By a more rigorous analysis, not involving the above stated simplifying assumptions that the molecule under consideration has a uniform velocity equal to that required by the kinetic equation and that the other molecules are stationary, it can be shown that the mean free path (for spherical molecules) is only 0.71 times as great as that computed by the above equation.

*Relations between the Diameter of the Molecules, the Number of Collisions, and the Mean Free Path. —*

\**Prob. 32.*—*a.* Considering, as illustrated in the figure, that a molecule of radius  $r$  is moving with a velocity  $u$  among stationary molecules, find an expression for the volume of the space within which the centers of the stationary molecules must be located in order that the moving molecule may collide with them during one second. *b.* Find an expression for the number of stationary molecules with which the moving molecule collides per second, in case a volume  $v$  of the gas contains  $n$  molecules uniformly distributed. *c.* Derive from this equation the expression given in the preceding text for the mean free path of the molecules, stating the reasons involved.

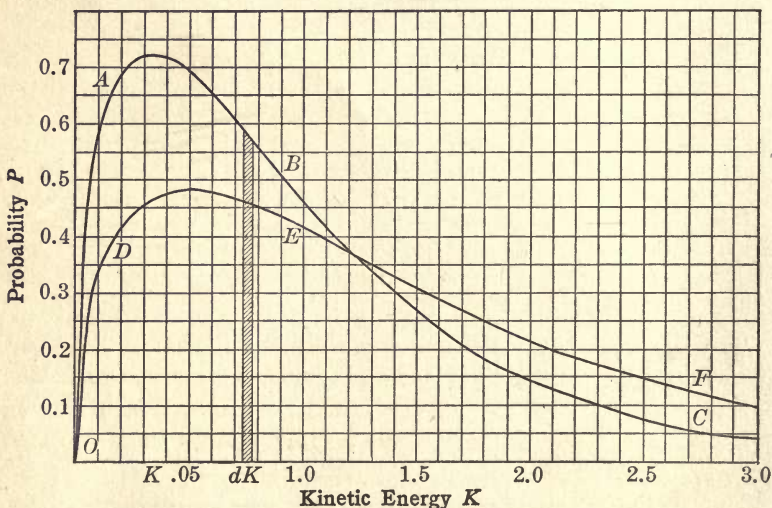


\**Prob. 33.*—From the diameters of the  $\text{CO}_2$  and  $\text{NH}_3$  molecules calculated in Prob. 31, find for the case that each gas is at  $20^\circ$  and 1 atm. the number of collisions made by one molecule per second, and the mean free path.

\*The mean free path is a factor that determines the magnitudes of certain properties of gases, especially of their viscosity and their electrical and thermal conductivities; and conversely, its own magnitude can be computed from the results of measurements of these properties. Since the number of collisions and the diameter of the molecules can be calculated from the mean free path by means of the equations given above, there are available a number of independent methods of determining all these molecular quantities.

**22. Distribution of the Velocities and Kinetic Energies of the Molecules of a Gas.**—It has been assumed thus far that all the molecules of a gas have the same velocity and kinetic energy. Evidently this cannot be the case, since as a result of the collisions there is a constant interchange of the kinetic energies, with consequent variation of their values from zero up to values much greater than the mean kinetic energy. It can be shown that, in view of the very

large number of molecules and the frequency of their collisions, their kinetic energies and velocities must be distributed in accordance with the laws of probability, of which the distribution of errors of observation around the mean value affords a familiar illustration. This law of the distribution of kinetic energies and velocities is known as the *Maxwell distribution law*.



The figure shows graphically the distribution of kinetic energies required by this law. The two graphs  $OABC$  and  $ODEF$  refer to  $0^\circ$  and  $136.5^\circ$ , corresponding to absolute temperatures which stand to each other in the ratio 2:3. As abscissas are plotted the kinetic energies  $K$  (equal to  $\frac{1}{2}mu^2$ ) of the molecules expressed in terms of the mean value of the kinetic energy at  $0^\circ$  as unity; and as ordinates are plotted the values  $P$  of such a function of  $K$  that the product  $P dK$ , represented by the area beneath any element of the graph, is equal to the fraction  $dn/\bar{n}$  of the whole number of molecules  $\bar{n}$  (in one mol) that have kinetic energies between  $K$  and  $K+dK$ ; the area beneath the whole graph being equal to unity and corresponding to the total number of the molecules. Otherwise interpreted, the product  $P dK$  is the fraction of the time that any given molecule has kinetic energies between  $K$  and  $K+dK$ . Correspondingly, the relative values of the ordinates  $P$ , for different points of the curve represent the relative fractions of all the molecules that have kinetic energies within any

definite infinitesimal amount of those represented by the corresponding abscissas  $K$ ; or they represent the relative fractions of the time that any one molecule has these kinetic energies. In the case of the graph  $OABC$ , where the kinetic energies are expressed in terms of the mean kinetic energy at the same temperature, the quantity  $P$ , commonly called the *probability function*, has the form

$$P = 2.07 K^{0.5} e^{-1.5K}.$$

*Prob. 34. — Fraction of the Molecules having Kinetic Energies between Definite Limits.* — Determine from the figure the percentages of the total number of molecules which at  $0^\circ$  have kinetic energies lying between limits which are multiples of the mean kinetic energy at  $0^\circ$ , as follows:  $a$ , 0.0 and 0.2;  $b$ , 0.2 and 0.6;  $c$ , 0.6 and 1.0;  $d$ , 1.0 and 2.0.

*Prob. 35. — Effect of Temperature on the Fraction of the Molecules having Kinetic Energies Greater than any Definite Absolute Value.* — Determine from the figure the percentages of all the molecules that,  $a$ , at  $0^\circ$ , and  $b$ , at  $136.5^\circ$ , have kinetic energies greater than twice the mean kinetic energy at  $0^\circ$ .

The fact, illustrated by the preceding problem, that the fraction of the molecules having kinetic energies exceeding any definite value increases rapidly with rising temperature is of much importance in relation to the effect of temperature on the vapor-pressure of liquid substances and on the rate of chemical reactions.

The graphs in the figure represent also the distribution of the squares of the velocities of the molecules in terms of the mean velocity-square at  $0^\circ$ . Similar graphs can be drawn to show the distribution of the velocities themselves. When the velocity  $u$  is expressed in terms of the square-root of the mean value of the velocity-square at the same temperature, the probability function has the form:

$$P = 4.14 u^2 e^{-1.5u^2}.$$

The percentages of the total number of molecules which possess values of the velocity that lie between limits which are certain multiples of the square-root of the mean velocity-square are as follows:

Velocity multiples	. . 0.0-0.4	0.4-1.4	1.4-2.5	2.5- $\infty$
Percentage of molecules	. . 8.2	76.9	12.7	2.2

\*Differential equations expressing the distribution of kinetic energies and velocities can readily be formulated as in Prob. 36. These equations cannot be directly integrated; but by methods of approximation the integrals have been evaluated between various limits.

*\*Prob. 36. — Expressions for the Fraction of the Molecules having Definite Kinetic Energies or Definite Velocities.* — With the aid of the probability-functions given in the text, formulate differential equations for the fraction  $dn/\bar{n}$  of the total number of molecules  $\bar{n}$  which possess, *a*, kinetic energies (expressed in terms of the mean kinetic energy) between any value  $K$  and an infinitesimally greater value  $K+dK$ ; and *b*, velocities (expressed in terms of the square-root of the mean velocity-square) between any value  $u$  and an infinitesimally greater value  $u+du$ .

\*Expressions for the fractions  $dn/\bar{n}$  and  $n_0/\bar{n}$  of the molecules that at any temperature  $T$  have absolute kinetic energies (1) between  $E$  and  $E+dE$ , and (2) greater than any definite value  $E_0$ , are given below. Equation (1) is obtained from that of Prob. 36*a* by replacing the energy-ratio  $K$  by the quantity  $E/\frac{3}{2}kT$  ( $\frac{3}{2}kT$  being the mean kinetic energy of the molecules); and equation (2) is obtained by integrating equation (1) between the limits  $E_0$  and  $\infty$ :

$$\frac{dn}{\bar{n}} = 1.13 \left( \frac{E}{kT} \right)^{\frac{1}{2}} e^{-\frac{E}{kT}} \frac{dE}{kT} \quad (1)$$

$$\frac{n_0}{\bar{n}} = 1.13 \left( \frac{E_0}{kT} \right)^{\frac{1}{2}} e^{-\frac{E_0}{kT}} \left( 1 + \frac{1}{2} \frac{kT}{E_0} - \frac{1}{4} \frac{(kT)^2}{E_0^2} + \dots \right) \quad (2)$$

\*The mean kinetic energy at any definite temperature is evidently directly related to the square-root of the mean velocity-square ( $\sqrt{\Sigma u^2/n}$ ) at the same temperature; this square-root being equal to the velocity derived from the kinetic equation  $\frac{1}{3}n m u^2 = NRT$ . In many kinetic relations the *most probable kinetic energy* and the *most probable velocity* are also important quantities. These are defined to be the kinetic energy and velocity, respectively, which the greatest number of molecules possess. Their values can be shown, as in Prob. 37, to stand in a definite numerical ratio to the mean values just mentioned. Thus the square of the most probable velocity is just two-thirds of the mean velocity-square. Another important quantity is the *mean velocity* ( $\Sigma u/n$ ), which can be shown by a less simple process to be 0.921 of the square-root of the mean velocity-square.

*\*Prob. 37. — Relations between the Most Probable and Mean Values of the Kinetic Energy and of the Velocity.* — *a.* Determine from the figure the ratio between the mean kinetic energy and the most probable kinetic energy. *b.* Derive this relation also from the probability-function given in the text, noting that the most probable kinetic energy corresponds to the maximum value of that function. *c.* Derive similarly the relation between the square-root of the mean velocity-square and the most probable velocity.

## III. THE ENERGY RELATIONS OF GASES

**23. Energy in General and the Law of its Conservation.** — The essential idea underlying the concept of *energy* is the constancy of a quantity which is involved in all the changes taking place in the universe; and this is often explicitly expressed by the statement that energy is neither created nor destroyed in any process whatever. This statement is called the *law of the conservation of energy*, or the *first law of thermodynamics*.

The law may be stated more concretely as follows: When a quantity of energy disappears at any place, a precisely equal quantity of energy simultaneously appears at some other place or places; and when a quantity of energy disappears in any form, a precisely equal quantity of energy simultaneously appears in some other form or forms; equal quantities of energy of different forms being understood to be such quantities as produce the same effect (for example, in modifying motion or raising temperature) when converted into the same form.

The exactness of this law has been established by many careful quantitative investigations made for the purpose. The law is also confirmed by the correspondence of the conclusions drawn from it with well-established facts and principles. Among these may be mentioned the following principle, which is a conclusion based upon the failure of many attempts to produce a contrary result: The production of an unlimited amount of work by a machine or arrangement of matter which receives no energy from the surroundings is an impossibility. An ideal process like that here stated to be impossible is sometimes called *perpetual motion of the first kind* (to distinguish it from another kind of perpetual motion which will be later described).

Of especial importance in chemical considerations are the energy effects attending changes in the state of systems. By the *system* is understood the definite kinds and quantities of matter under consideration. A system is said to be in a definite *state* when the temperature, pressure, state of aggregation, quantity, and chemical composition of each of its parts is fixed; and a change in any of these conditions is called a *change in the state of the system*. Thus the system under consideration might consist of 16 g. of the element oxygen and 2.015 g. of the element hydrogen. This system might exist initially in the state of a mixture of 0.5 mol of oxygen gas ( $O_2$ ), and 1 mol of hydrogen gas ( $H_2$ ) at a temperature of  $20^\circ$  and a total pressure of ten

atmospheres. It might now undergo a change in state, and exist finally in the state of one formula-weight of liquid water at  $20^{\circ}$  and one atmosphere.

It follows from the law of the conservation of energy that, when the state of a system is fixed, its energy-content  $U$  is also fixed; and therefore also that any change in the state of a system is attended by a definite change  $\Delta U$  in its energy-content (equal to the difference  $U_2 - U_1$  between its energy-content in the two states), whatever be the process by which the change takes place. This corollary from the law of the conservation of energy, stating that the change in the energy-content of a system is determined solely by its initial and final states, is of so much importance in chemical considerations that it has received a special name — the *law of initial and final states*.

Corresponding to the change in the energy-content of the *system*, there must, of course, be an energy effect in the *surroundings*; and, in general, the only method of determining the change in the energy-content of a system is to measure the energy produced in the surroundings. This is ordinarily done by causing the change in state to take place within a calorimeter and measuring the heat which is imparted to or withdrawn from the calorimeter and its contents; account being taken of any other form of energy which may at the same time be produced or destroyed.

The energy lost or gained by the system may appear or disappear in the surroundings in any of its various forms; but in energy considerations it is primarily important only to differentiate the production of *heat* from that of the other forms of energy. Such other forms of energy (that may be associated with matter) are collectively designated *work*. Under this term are included, for example, production of motion in a body, displacement of a force through a distance, change of volume under pressure, development of electrical energy, and production of chemical changes. All these forms of work are quantitatively transformable into one another; but the transformation of heat into work is subject to certain limitations, which will be considered later. It is for this reason that heat and work are differentiated from each other. It will be noted that the term work is here used in a broader sense than that in which it is used in the science of mechanics.

With the aid of the concepts of energy-content, heat, and work, the law of the conservation of energy may now be expressed by the statement that the decrease in the energy-content of the system

when it undergoes a change in state is equal to the sum of the quantities of heat and work produced in the surroundings. Of these three quantities the change in energy-content is most fundamental, since it has a definite value for any definite change in state; while the quantities of heat and of work produced may vary with the process by which the change in state takes place.

Three units of energy are commonly used in scientific work — the erg, the joule, and the calorie. The *erg* is the energy expended when a force of one dyne is displaced through one centimeter, or it is twice the energy possessed by a mass of one gram when moving with a velocity of one centimeter per second. The *joule* is a decimal multiple of the erg; namely, one joule equals  $10^7$  ergs. The *mean calorie* is one-hundredth part of the heat required to raise one gram of water from  $0^\circ$  to  $100^\circ$ . This is identical within 0.02% with the *ordinary calorie*, which is the heat required to raise one gram of water from  $15^\circ$  to  $16^\circ$ . One calorie (1 cal.) is equal to 4.182 (approximately 4.18) joules, or  $4.182 \times 10^7$  ergs, this value being the so-called mechanical equivalent of heat.

*Prob. 38. — Evaluation of the Change in Energy-Content.* — When 1 g. of liquid water is vaporized at  $100^\circ$  against a pressure of 1 atm., the heat withdrawn from the surroundings is 537 cal., and the work produced by the expansion against the constant pressure is 168 joules.

- In which state does the water have the greater energy-content, and what is the difference between the two energy-contents in calories?
- How much heat would be drawn from the surroundings in case 1 g. of liquid water at  $100^\circ$  and 1 atm. was vaporized within a closed vessel (no work being produced in the surroundings) so as to form water-vapor at  $100^\circ$  and 1 atm?

**24. Work Attending Volume Changes in General.** — The work produced when a system changes its volume is of especial importance in chemical considerations. It is most readily derived for the case that the volume undergoes a change in dimensions in one direction only. Suppose that a liquid or gaseous substance contained in a cylinder is enclosed by a movable piston of cross-section  $a$ , and that a force  $f$  is exerted upon this piston, for example, by a weight placed upon it. Suppose now that the piston rises through a distance  $dl$ . The increase of volume  $dv$  is then  $adl$ , and the force acting upon the unit of surface, which force is the *pressure*  $p$ , is  $f/a$ . The work  $dW$  produced by the expansion is therefore given by the equations:

$$dW = f dl = p a dl = p dv.$$

That is, the work is equal to the product of the pressure into the infinitesimal increase of volume that takes place. It can be easily demonstrated that this equation also holds true in the general case in which the volume increases in dimensions in any number of directions.

The general expression for the work produced when a body undergoes a change of volume from  $v_1$  to  $v_2$ , is therefore:

$$W = \int_{v_1}^{v_2} p \, dv. \quad = \quad p(v_2 - v_1)$$

In order to carry out the integration it is evidently necessary to know how the pressure varies with the volume of the system as the change in state under consideration takes place.

The most common case in energy discussions is that in which the external pressure is considered to be substantially equal to the pressure exerted by the substance or substances of which the system is composed, these two pressures differing by only the infinitesimal amount which in the absence of friction suffices to cause the change in state to take place. In this case, in order to carry out the integration, it is necessary to know the functional relation between the pressure and the volume of the substance or substances involved, — in other words, to know the equation of state of the substance or mixture of substances of which the system consists.

*Prob. 39. — Work Produced by the Change in Volume of a System at Constant Pressure. — a.* Calculate the work in ergs and calories that is produced when one formula-weight of water ( $\text{H}_2\text{O}$ ) vaporizes at  $100^\circ$  against the pressure of 1 atm. The specific volume of liquid water at  $100^\circ$  is 1.043, and that of saturated water vapor is 1650. *b.* Find the percentage errors that would be made by neglecting the volume of the liquid, and by regarding the vapor as a perfect gas. *c.* Formulate a general expression for the work produced when a system undergoes a change of volume under a constant pressure; and show that under these approximate assumptions the work  $W$  produced by the vaporization at a constant temperature  $T$  of that quantity of a liquid which forms  $N$  mols of saturated vapor is given by the expression  $W = NRT$ . *d.* Show that the value of the gas-constant  $R$  is 1.985 cal. per degree.

*Prob. 40. — Work Producing by the Change in Volume and Pressure of a Perfect Gas at Constant Temperature. — a.* Calculate the work in calories produced when 1 mol of a perfect gas at 2 atm. expands at  $20^\circ$  till its pressure becomes 1 atm., the opposing external pressure being kept always substantially equal to that of the gas. *b.* Calculate the work in calories produced when under these conditions 1  $\text{CO}_2$  at 2 atm. expands at  $20^\circ$  till its pressure becomes 1 atm. The molal volume of  $\text{CO}_2$  at  $20^\circ$  and 2 atm. is 11,890 ccm. (or 1.16% less than that of a perfect gas). *Ans. b,* 408 cal.

**25. The Energy-Content of Systems in General in Relation to Temperature and Heat-Capacity.** — The change in the energy-content which attends a change in the temperature of any system is experimentally determined by measuring the quantities of heat and work withdrawn from or imparted to the surroundings. The ratio of the quantity of heat  $dQ$  absorbed when the temperature of the system rises from  $T$  to  $T+dT$  to the rise of temperature  $dT$  is called its *heat-capacity*  $C$  at  $T$ ; that is,  $C=dQ/dT$ . The heat-capacity is substantially equal to the quantity of heat absorbed when the temperature rises one degree. When the heating takes place without change of pressure, the heat absorbed per degree is called the *heat-capacity at constant pressure*  $C_p$ . When the heating takes place without change of volume, the heat absorbed per degree is called the *heat-capacity at constant volume*  $C_v$ . The heat-capacity of any homogeneous system is obviously the product of its weight by the heat-capacity of one gram of it, which is called its *specific heat-capacity*  $C$  (or often its specific heat). The heat-capacity of one mol or one formula-weight of a pure substance is called its *molal or formal heat-capacity*  $\tilde{C}$ . The heat-capacity of one atomic weight is called the *atomic heat-capacity*.

*Prob. 41. — Measurement of the Heat-Capacity of Gases.* — Through a coil within a water calorimeter at  $20.000^\circ$  having a total heat-capacity of 1100 cal. per degree 11.0 g. of carbon dioxide preheated to various temperatures were passed at a pressure of 1 atm. in a series of experiments, and the rise in temperature in the calorimeter was measured, with the following results:

Initial gas temperature . . .	$200^\circ$	$400^\circ$	$600^\circ$	$800^\circ$
Final calorimeter temperature	$20.389^\circ$	$20.861^\circ$	$21.378^\circ$	$21.930^\circ$

*a.* Calculate the quantity of heat given off to the calorimeter in each experiment. *b.* Plot on a large scale these heat quantities  $Q$  as ordinates against the initial gas temperatures  $t$  as abscissas. *c.* Determine with aid of the plot the molal heat-capacity of carbon dioxide at  $200^\circ$  and that at  $600^\circ$ .

When a system is heated without change of volume, no work is produced, and the change in its energy-content per degree is therefore simply equal to the heat absorbed from the surroundings or to the heat-capacity of the system at constant volume.

When a system is heated at constant pressure, not only is heat absorbed from the surroundings, but also work is produced in them. The increase in energy-content per degree is therefore equal to the heat absorbed diminished by the work produced.

*\*Prob. 42. — Mathematical Expressions for the Heat-Capacities. —* Formulate partial-derivative expressions for the definitions of the heat-capacity at constant volume and that at constant pressure, and for the relation of each of these heat-capacities to the corresponding change in energy-content per degree.

$$\text{Ans. } C_v = \left( \frac{\partial Q}{\partial T} \right)_v ; \text{ etc.}$$

**26. The Energy-Content and Heat-Capacity of Perfect Gases. —** Experiments have shown that when a perfect gas expands at a constant temperature without producing any work (for example, when it expands within a calorimeter from one vessel into another vessel previously evacuated), there is no heat-effect in the surroundings (no change of temperature in the calorimeter). Such experiments have established the important law that the energy-content of a definite quantity of a perfect gas at any definite temperature has the same value, whatever be its volume and pressure. In other words, for the change in state which occurs when a perfect gas changes its volume and pressure at a constant temperature, the change  $\Delta U$  in its energy-content is zero.

From this law of perfect gases the following principles can be derived with aid of the law of initial and final states, as in Probs. 43 and 44:

(1) At any definite temperature the increase per degree  $dU/dT$  of the energy-content of any definite quantity of a perfect gas has the same value whatever be the initial and final pressures and volumes; and therefore the heat-capacity at constant volume of any perfect gas is independent of the pressure and volume.

(2) The molal heat-capacity of a perfect gas at constant pressure is greater than that at constant volume by an amount equal in value to the gas-constant  $R$ , whatever be the gas and whatever be the temperature or pressure; that is,

$$\tilde{C}_p - \tilde{C}_v = R = 1.985 \text{ cal. per degree.}$$

*Derivation of the Heat-Capacity Relations of Perfect Gases. —*

*Prob. 43. —* Derive the first principle stated in the preceding text by considering that a perfect gas changes by two different processes from a volume  $v_1$  at pressure  $p_1$  and temperature  $T_1$  to a volume  $v_2$  at pressure  $p_2$  and temperature  $T_2$ .

*Prob. 44. —* Derive the second principle stated in the preceding text by a consideration similar to that employed in the last problem.

This second principle obviously enables the heat-capacity at constant volume to be calculated from the heat-capacity at constant

pressure. This is of importance, since the former quantity is one which it is difficult to determine accurately by direct experiment, owing to the fact that any rigid container used for holding the gas and preventing its expansion has unavoidably a much larger heat-capacity than the gas itself; while the latter quantity can be readily and accurately measured (as illustrated by Prob. 41).

In view of this difficulty of determining directly the heat-capacity at constant volume, it is important to note also that the *heat-capacity ratio*  $C_p/C_v$  can be derived from measurements of certain properties of gases; especially, from measurements of the change of pressure which results when the gas expands *adiabatically* (that is, without imparting heat to the surroundings or withdrawing heat from them), and from measurements of the velocity of sound through the gas. These methods need not, however, be here described.

**27. The Heat-Capacity of Perfect Gases in Relation to their Molecular Composition.** — The heat-capacity of perfect gases depends primarily on the complexity of their molecules, as is shown by the following principles.

The molal heat-capacity at constant volume  $\tilde{C}_v$  has the smallest value for gases with monatomic molecules, such as mercury, helium, and argon; and it has the same value, namely  $\frac{3}{2}R$  or 2.98 cal. for all such gases at all temperatures. The corresponding value of  $\tilde{C}_p$  is  $\frac{5}{2}R$  or 4.96 cal. It will be shown in Art. 28 that the kinetic theory affords a striking explanation of this simple behavior.

The behavior of gases with diatomic molecules is less simple. Many of these gases, for example those with the formulas  $N_2$ ,  $O_2$ ,  $CO$ ,  $NO$ ,  $HCl$ , have substantially the same value of  $\tilde{C}_v$ , and one which varies appreciably, but not very greatly, with the temperature, between  $0^\circ$  and  $1200^\circ$ ; thus for all these gases the value of  $\tilde{C}_v$  is 4.9 cal. at  $20^\circ$ , 5.6 cal. at  $1000^\circ$ , and 6.3 cal. at  $2000^\circ$ . Between the temperatures  $0^\circ$  and  $-180^\circ$  the values for these gases change irregularly, but not very greatly; thus at  $-180^\circ$ ,  $\tilde{C}_v$  is 4.73 for nitrogen, 4.91 for oxygen, and 4.76 for carbon monoxide. The values for hydrogen ( $H_2$ ) between  $20^\circ$  and  $2000^\circ$  are slightly (about 0.15 cal.) smaller than those for the gases just mentioned, and they become very much smaller at very low temperatures, attaining at  $-180^\circ$  the value 4.3 cal., and at  $-210^\circ$  the value 3.0 cal. shown by monatomic gases, this value then remaining constant at any rate down to  $-240^\circ$  ( $33^\circ A.$ ). A few diatomic gases, for example those with the formulas  $Cl_2$ ,  $Br_2$ ,  $I_2$ ,  $ICl$ , have at room

temperature larger values of  $\tilde{C}_v$  than do the other diatomic gases; thus the value for chlorine is 5.9 cal. at  $20^\circ$ .

The only general statements that can be made in regard to the heat-capacities of triatomic and other polyatomic gases are that the values are much larger than those for the diatomic gases, that they increase more rapidly with the temperature, and that they increase with the complexity of the molecule; thus the values of  $\tilde{C}_v$  at  $200^\circ$  are 6.5 for water vapor ( $\text{H}_2\text{O}$ ), 8.5 for carbon dioxide ( $\text{CO}_2$ ) and sulfur dioxide ( $\text{SO}_2$ ), 7.4 for ammonia ( $\text{NH}_3$ ), and 41.6 for ether ( $\text{C}_4\text{H}_{10}\text{O}$ ).

The following table shows the functions which express, in general within one or two percent, the observed values of the molal heat-capacities at constant volume at atmospheric pressure, of some of the common gases at various temperatures.

MOLAL HEAT-CAPACITIES AT CONSTANT VOLUME

Substances	Range of temperature	Value of $\tilde{C}_v$
He, Ne, A } Hg, Na, K }	Complete	$2.98 + 0.00 T$
$\text{N}_2, \text{O}_2, \text{CO}$ } $\text{NO, HCl}$ }	$0 - 2000^\circ$	$4.70 + 0.0007 T$
$\text{H}_2$	$0 - 2000^\circ$	$4.55 + 0.0007 T$
$\text{Cl}_2$	$0 - 2000^\circ$	$5.65 + 0.0007 T$
$\text{NH}_3$	$0 - 500^\circ$	$5.83 + 0.0026 T + 0.0000012 T^2$

These principles in regard to heat-capacity, especially that relating to monatomic gases, have made it possible to determine (as illustrated in Prob. 45) the atomic weight of the inert elements, helium, neon, argon, etc., to which, because of their failure to form compounds, the usual method described in Art. 14 is not applicable.

*Prob. 45. — Determination of Atomic Weight from the Heat-Capacity Ratio.* — From the experimentally determined velocity of sound in argon gas the heat-capacity ratio  $C_p/C_v$  has been found to be 1.67. Find the atomic weight of argon by combining this result with its density, which at  $20^\circ$  and 1 atm. has been found to be 1.246 times as great as that of oxygen; stating the principles involved.

**28. The Energy-Content and Heat-Capacity of Perfect Gases in Relation to the Kinetic Theory.** — In the discussion of the kinetic theory in Art. 18 only the *translatory kinetic energy* of the molecules (that due to their linear motion) was considered. It is evident, however, that the molecules may be set in rotation as a result of their collisions, and consequently that they may possess *rotational kinetic*

energy. It is evident also that the atoms within the molecules may possess kinetic energy due to vibration and potential energy arising from forces acting between the atoms and dependent upon their position with reference to one another; these constituting the *atomic energy* of the molecules. The proportion which each of these three kinds of energy contributes to the total energy of the molecules may be expected to vary with the temperature and with the nature of the molecules.

In the case of monatomic molecules the conditions are simpler. For in the first place, since the molecule is identical with the atom, the atomic energy falls away. In the second place, it may well be true that the atoms, and hence also the molecules, are so small or so symmetrical that their kinetic energy of rotation is negligible in comparison with their kinetic energy of translation. In this case the energy-content of the gas would consist solely in the translatory kinetic energy  $K$  of its molecules. And the heat-capacity  $C_v$  at constant volume, which was shown in Art. 25 to be equal in general to the increase  $dU/dT$  in the energy-content per degree, would be equal to the increase  $dK/dT$  in this kinetic energy per degree; which increase  $dK/dT$  has been shown in Art. 18 to be equal to  $\frac{3}{2}R$  or 2.98 cal. per degree for one mol of any gas. Now, experimental determinations have in fact shown, as stated in Art. 27, that all monatomic gases have a molal heat-capacity at constant volume substantially equal to 2.98 cal. per degree. The conformity of this prediction of the kinetic theory with the facts is one of the striking successes of the theory.

The fact stated in Art. 27 that most of the diatomic gases (nitrogen, oxygen, carbon monoxide, etc.) have values of  $\tilde{C}_v$  which are nearly the same (about 5.0 cal. at 20°) for the different gases and which do not vary much with the temperature indicates that the atomic energies and rotational energy of their molecules increase in nearly the same proportion as the translatory kinetic energy. The fact, however, that the heat-capacity of hydrogen gas, though not differing greatly from that of the other gases at room temperature, attains the value for a monatomic gas at very low temperatures, suggests that its molecules are then no longer taking up an appreciable proportion of atomic or rotational energy.

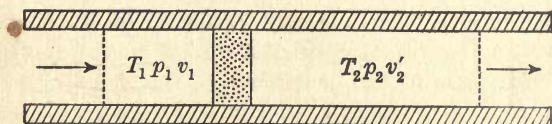
Diatomic gases like chlorine which have larger values of  $\tilde{C}_v$  utilize this greater amount of absorbed heat to set their atoms into more rapid vibration and to separate them further from each other. This

is in correspondence with the lower temperatures at which the molecules of these latter gases dissociate into their atoms.

The molecules of gases with more than two atoms may be expected to take up more energy of rotation than the more nearly two-dimensional diatomic molecules and to convert more of the absorbed heat into atomic energy. This is in accordance with the fact that in general the heat-capacity increases with the complexity of the molecule.

**29. The Energy-Content of Imperfect Gases in Relation to Volume and Pressure.** — Actual gases show deviations from the perfect-gas law that the energy-content of the gas at any definite temperature is independent of its volume and pressure. These deviations always lie in the direction that the energy-content of the gas increases with decrease in its pressure. They are small at atmospheric pressure, increase rapidly with the pressure, and become large at 30-100 atmospheres.

The increase in energy-content attending an isothermal expansion is most accurately determined by *porous-plug experiments*, in which the gas is caused to flow continuously through a well-insulated tube containing a plug of porous material, as illustrated in the figure.



Under these conditions the gas expands without taking up heat from the surroundings and without producing work, except that equivalent to the change in its pressure-volume product. It undergoes thereby a decrease in temperature, which is often called from its discoverers the *Joule-Thomson effect*. This decrease in temperature is accurately measured; and from its magnitude, from the heat-capacity of the gas, and from the change in its pressure-volume product, the increase in the energy-content that would have attended an isothermal expansion is calculated, in the way illustrated by the following problem.

*\*Prob. 46. — Determination of the Change in Energy-Content by Porous-Plug Experiments.* — Carbon dioxide at pressure  $p_1$  (e.g., 2 atm.) and temperature  $T_1$  (e.g., 20.00°) is caused to flow continuously through a well-insulated hardwood tube containing a porous plug of cotton. On passing through the plug its pressure falls to  $p_2$  (e.g., 1 atm.), and it emerges from the tube at this pressure. After the gas has flowed so

long that every part of the apparatus has assumed the temperature of the gas in contact with it, the expansion of the gas takes place without exchange of heat with the surroundings. Its temperature after passing through the plug is found to be  $T_2$  (e.g.,  $18.86^\circ$ ). These conditions are illustrated by the figure. *a.* What other process must be combined with this adiabatic process in order that the net result of the two processes may be the isothermal expansion of one mol of the gas from pressure  $p_1$  to pressure  $p_2$  at a temperature  $T_1$ ? *b.* Formulate expressions for the work produced  $W$ , the heat absorbed  $Q$ , and the change in energy-content  $\Delta U$ , for each of these two processes. (Note that in the first process a volume  $v_1$  of the gas disappears on one side of the plug under a constant pressure  $p_1$ , and that a certain volume  $v_2'$  of the gas is produced on the other side of the plug under a constant pressure  $p_2$ .) *c.* Combine these results so as to give an expression for the change in energy-content that attends a change in pressure from  $p_1$  to  $p_2$  of one mol of the gas at a constant temperature  $T_1$ . *d.* Calculate in calories the change in energy-content attending the expansion of 1 mol of carbon dioxide from a pressure of 2 atm. to a pressure of 1 atm. at  $20^\circ$ , using the following data in addition to those given above: the molal volume of carbon dioxide at  $20^\circ$  and 2 atm. is 11,890 ccm., and at  $20^\circ$  and 1 atm. is 23,920 ccm.; its molal heat-capacity at  $20^\circ$  and at a constant pressure of 1 atm. is 8.92 cal. per degree. *e.* Calculate the heat that would be absorbed from the surroundings if the change in state given in *d* took place at  $20^\circ$  against an opposing pressure kept substantially equal to that of the gas, using the result obtained in Prob. 40b. *Ans. d, 6.78 cal.*

At high pressures and at low temperatures the Joule-Thomson cooling effect and the corresponding increase in energy-content attending isothermal expansion are large even in the case of difficultly condensible gases. Thus, when air at 2 atmospheres and at  $20^\circ$  expands to a pressure of one atmosphere under the conditions of a porous-plug experiment, there is a fall of temperature of  $0.25^\circ$ ; but if the initial pressure is 102 atmospheres there is a fall of  $25^\circ$  when the initial temperature is  $0^\circ$ , and a fall of temperature of  $74^\circ$  when the initial temperature is  $-100^\circ$ .

Certain technical processes for liquefying air (for example, the Linde process) utilize only the Joule-Thomson effect, but certain other processes (such as the Claude process) provide for production of work during the expansion, whereby a greater cooling effect is obtained (as indicated by Prob. 46e).

**\*30. The Energy-Content of Imperfect Gases at Constant Temperature in Relation to the Kinetic Theory.** — The increase in energy-content attending the isothermal expansion of a gas, as computed from porous-plug experiments like those described in Art. 29, is evidently

equivalent to the energy that must be imparted to the gas in order to separate its molecules from one another. In other words, it is equal to the internal work that has to be done in displacing the cohesion pressure through the increment of volume. It follows therefore that the increase  $dU$  in energy-content attending an increase in volume  $dv$ , and the increase  $\Delta U$  in energy-content attending an increase in volume from  $v_1$  to  $v_2$ , will be given, if the cohesion pressure has the value required by the van der Waals equation, by the following expressions:

$$dU = \frac{aN^2}{v^2} dv; \text{ or } \Delta U = aN^2 \left( \frac{1}{v_1} - \frac{1}{v_2} \right); \text{ or (for one mol) } \Delta \tilde{U} = a \left( \frac{1}{\tilde{v}_1} - \frac{1}{\tilde{v}_2} \right).$$

*Prob. 47. — Calculation of the Change in Energy-Content from the Cohesion-Constant.* — Calculate the increase in energy-content in calories attending the isothermal expansion of  $\text{1CO}_2$  from 2 atm. to 1 atm. at  $20^\circ$ , from the value of the cohesion-constant for carbon dioxide given in Prob. 28, and tabulate this value beside that derived in Prob. 46 from the data of porous-plug experiments.

Conversely, the cohesion-constant can be derived from the results of porous-plug experiments. And in general the so-obtained values of this constant are approximately identical with those calculated from the pressure-volume relations by the van der Waals equation. Thus the cohesion-constant for carbon dioxide may be calculated from the data of Prob. 46 to be  $6.62 \times 10^6$ , while that derived from the pressure-volume relations is  $6.23 \times 10^6$ . This agreement shows that the term  $aN^2/v^2$  in the van der Waals equation does in reality correspond to a cohesion pressure arising from an attraction between the molecules.

## CHAPTER III

### THE MOLAL PROPERTIES OF SOLUTIONS AND THE MOLECULAR THEORY

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#### I. VAPOR-PRESSURE AND BOILING-POINT IN GENERAL

**31. Vapor-Pressure.** — A liquid in contact with a vacuous space vaporizes until the pressure of its vapor in that space attains a perfectly definite value which is determined by the nature of the liquid and by the temperature. If, on the other hand, vapor having a pressure greater than this definite value is brought into contact with the liquid, condensation occurs until the pressure of the vapor falls to that value. In other words, for a given liquid at a given temperature there is only one pressure which its vapor can have and exist in equilibrium with that liquid. This pressure is called the *vapor-pressure* of the liquid. This is to be distinguished from the pressure of the vapor, which when not in contact with the liquid may have any value from zero up to one somewhat exceeding the vapor-pressure. Solids likewise have definite vapor-pressures, which with certain substances (like iodine) are appreciable even at room temperature.

The vapor-pressure of a liquid or solid substance increases rapidly with increasing temperature, as illustrated by the data of Prob. 3.

When a liquid or solid is in contact with a space containing a gas (for example, when water or iodine is in contact with an air space), approximately the same quantity of the liquid or solid vaporizes as if the gas were not present, provided the gas is only slightly soluble in the liquid, and provided its pressure is not much greater than one atmosphere. When the gas is readily soluble in the liquid, or when its pressure is large, considerable deviations from this principle may result.

*Prob. 1. — Pressure-Volume Relations of Wet and Dry Gases.* — 25 ccm. of dry air at  $28^{\circ}$  and 1 atm. are collected over water, whose vapor-pressure at  $28^{\circ}$  is 28 mm. *a.* What is the pressure if the volume is still 25 ccm.? *b.* What is the volume if the pressure is 1 atm.? *Ans. b,* 25.95.

*Prob. 2. — Air-Bubbling Method of Determining Vapor-Pressure.* — 2000 ccm. of dry air at  $15^{\circ}$  and 760 mm. are bubbled through bulbs containing a known weight of carbon bisulfide ( $\text{CS}_2$ ) at  $15^{\circ}$ , and the mixture of air and bisulfide vapor is allowed to escape into the air at a

pressure of 760 mm. By reweighing the bulbs, 3.011 g. of the bisulfide are found to have vaporized. Find the vapor-pressure of carbon bisulfide at 15°. *Ans.* 242 mm.

*Steam-Distillation of Liquids Insoluble in Water. —*

*Prob. 3.* — Steam is bubbled through chlorbenzene ( $\text{C}_6\text{H}_5\text{Cl}$ ) in a distilling flask; and the vapors, which escape under a barometric pressure of 1 atm., are condensed as a distillate. The steam partially condenses in the distilling flask, and brings the mixture of water and chlorbenzene (which are not appreciably soluble in one another) to that temperature where equilibrium prevails between each liquid and its vapor. Determine this temperature and the molal composition of the distillate with the aid of a plot of the following data, which represent the vapor-pressures of the pure substances at various temperatures:

	70°	80°	90°	100°
Water . . . . .	234	355	526	760 mm.
Chlorbenzene . . . .	98	145	208	292 mm.

*Prob. 4.* — A current of steam is passed at atmospheric pressure through a mixture of water and nitrobenzene ( $\text{C}_6\text{H}_5\text{NO}_2$ ). Calculate, *a*, the temperature of the distilling mixture, and, *b*, the percentage by weight of nitrobenzene in the distillate, from the following data: the vapor-pressure of water at 100° is 760 mm. and changes by 3.58% per degree; that of nitrobenzene at 100° is 20.9 mm. and changes by 5.0% per degree. *Ans. b*, 15.5%.

**32. Relation of Boiling-Point to Vapor-Pressure.** — The *boiling-point* of a liquid is the temperature at which it is in equilibrium with its vapor when both are subjected to any definite external pressure. In other words, it is the temperature at which the vapor-pressure, which increases as the temperature rises, becomes equal to the external pressure. When this temperature is exceeded by an infinitesimal amount, assuming that there is no superheating, the vapor forms throughout the mass of the liquid (not merely at its free surface), giving rise to the familiar phenomenon of boiling.

*Prob. 5.* — *Change of Boiling-Point with Barometric Pressure.* — The vapor-pressure of water at 100° increases 27.2 mm. per degree. What variation of its boiling-point corresponds to a variation of the barometric pressure from 730 to 790 mm.?

**33. Change of Vapor-Pressure with Temperature. The Clapeyron Equation.** — The vapor-pressure of liquids or solids increases very rapidly with the temperature, and roughly by equal multiples of its value for equal increments of temperature.

*Prob. 6.* — *Approximate Relation between Vapor-Pressure and Temperature.* — From the data of Prob. 3 find and tabulate the ratios of the

vapor-pressure at 80° and 70°, 90° and 80°, and 100° and 90°, *a*, for water; and *b*, for chlorbenzene.

From the laws of thermodynamics, there can be derived, as shown in Art. 165, an exact differential expression for the increase of the vapor-pressure  $p$  of a liquid or solid at the absolute temperature  $T$  with the temperature. This expression, which is known as the *Clapeyron equation*, is as follows:

$$\frac{dp}{dT} = \frac{\Delta H}{T \Delta v}.$$

In this equation  $\Delta v$  represents the increase in volume when any definite quantity of the substance changes at the pressure  $p$  and temperature  $T$  from the state of liquid or solid to the state of saturated vapor, and  $\Delta H$  denotes the heat absorbed from the surroundings when this quantity of substance undergoes the same change in state. This quantity of heat is commonly called the *heat of vaporization*, or when referred to one mol of the substance, its *molal heat of vaporization*.

Since at the boiling-point of a liquid its vapor-pressure is equal to the external pressure upon the liquid and vapor, the Clapeyron equation also expresses (more clearly in the inverted form) the change of boiling-point with the external pressure.

In numerical applications of this equation, the energy quantities  $\Delta H$  and  $\Delta v \times dp$  must be expressed in corresponding units. The latter quantity will be in ergs when the volumes are in cubic centimeters and the pressure is in dynes per square centimeter. The units of energy commonly employed and the relations between them were described in Art. 23.

*Prob. 7. — Application of the Clapeyron Equation. — a.* Calculate with the aid of the Clapeyron equation the volume of one mol of saturated water-vapor at 100° from the following data: At 100° the vapor-pressure of water increases 27.2 mm. per degree, the heat of vaporization of one gram of it is 537 cal., and the specific volume of liquid water is 1.043. *b.* Calculate by the perfect-gas equation the volume of one mol of saturated water-vapor at 100°. *c.* By comparing these two values of the molal volume, determine the percentage error that would be made in assuming that the saturated vapor conforms to the perfect-gas law. *Ans. a*, 29920 ccm.; *c*, 2.3%.

A simpler, but less exact form of the Clapeyron equation can be derived (as in Prob. 8) by making the assumptions that the volume of the liquid or solid is negligible in comparison with that of the

saturated vapor and that the vapor conforms to the perfect-gas laws. This *approximate Clapeyron equation* is

$$\frac{d \log p}{dT} = \frac{\Delta \tilde{H}}{RT^2}.$$

In this equation  $p$  denotes the vapor-pressure of the liquid or solid substance at the absolute temperature  $T$ ,  $\Delta \tilde{H}$  its molal heat of vaporization at that temperature, and the symbol  $\log$  the natural logarithm (to the base  $e$ ). (This symbol is always used in this sense in this book; logarithms to the base 10 being denoted by the symbol  $\log_{10}$ . It may be noted that  $\log x = 2.3026 \log_{10} x = \text{approximately } 2.3 \log_{10} x$ .)

The approximate Clapeyron equation evidently yields, at moderate pressures where the volume of the liquid may usually be neglected, values of  $dp/dT$  or of  $d \log p/dT$  which are less than those derived from the exact equation by nearly the same percentage amount as the actual volume of the saturated vapor is less than that calculated by the perfect-gas equation, or by the same percentage amount as the actual value of  $p v$  for one mol of the saturated vapor is less than that of  $RT$ . This amount, for example, is 2.3% for water at  $100^\circ$  (as found in Prob. 7), and 3.6% for ethyl alcohol at  $78.3^\circ$  (its boiling-point at one atmosphere). These quantities are evidently the values of the deviation-coefficient  $\alpha$  for these vapors in the equation of state for gases at moderate pressures, given in Art. 15.

The approximate Clapeyron equation can be integrated, usually without much error, between any two temperatures not greatly different from each other under the assumption that the heat of vaporization is constant between those temperatures, as illustrated in Prob. 9.

*Prob. 8. — Derivation of the Approximate Clapeyron Equation. —*

- a.* From the exact Clapeyron equation derive the approximate form given in the text with the aid of the simplifying assumptions there mentioned.
- b.* From the results of Prob. 7 find the percentage error in  $dp/dT$  that would result from neglecting the volume of the liquid in the case of water at  $100^\circ$ .
- c.* Show that, aside from the correction for the volume of the liquid, the percentage error in  $dp/dT$  as calculated by the approximate equation is equal to the percentage difference between  $RT$  and the actual value of  $p v$  for one mol of the saturated vapor.

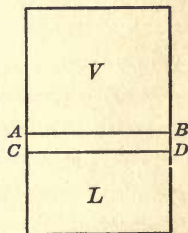
*Prob. 9. — Integration of the Approximate Clapeyron Equation. —*

- a.* Integrate the approximate Clapeyron equation so as to obtain a relation between the vapor-pressures  $p_1$  and  $p_2$  at two different temperatures  $T_1$  and  $T_2$ , assuming that the heat of vaporization does not vary between

the two temperatures. *b.* Calculate by the equation so obtained the boiling-point of water at 92.0 mm., and its vapor-pressure at 75°. *c.* The actual boiling-point at 92.0 mm. is 49.88°, and the actual vapor-pressure at 75° is 289.3 mm. State what inexact assumptions are involved in the equation which would account for the divergence.

**34. Vaporization in Relation to the Kinetic Theory.** — When a liquid is placed in communication with an empty space, its molecules, which according to the kinetic theory are continually in motion, will escape from its surface into the space above it till the vapor attains such a pressure that the number of molecules entering the liquid surface from the vapor side becomes equal to the number of molecules leaving the surface from the liquid side. When this occurs a stationary condition of equilibrium is evidently established, and the then prevailing pressure of the vapor represents the vapor-pressure of the liquid.

The kinetic principles underlying vaporization may be more fully developed by considering what determines the number of molecules that pass through the surface in the two directions. In the figure the line *AB* represents an imaginary plane above which the vapor *V* may be regarded as homogeneous, and the line *CD* represents another imaginary plane below which the liquid *L* may be regarded as homogeneous. In the intervening region *ABCD*, constituting the surface layer of the liquid, which in reality is of molecular dimensions, there is a progressive increase in the number of molecules per unit-volume from the number present in the vapor to the number present in the liquid.



Now the molecules in the vapor, assuming it to be a perfect gas, exert no attraction upon one another; but between the molecules of the liquid, as between those of a gas at high pressure (Art. 20), there is a large attraction. Within the main body of the liquid (below *CD*) there is, to be sure, no resultant attraction on any given molecule, since it is attracted equally in all directions by the uniformly distributed molecules surrounding it; but any molecule in the surface layer will evidently be attracted downwards (into the liquid) in consequence of the greater density of the molecules in the layers below it. All the molecules that strike the plane *AB* from above (that is, from the vapor side) will therefore have their downward velocities increased

by the attraction and will pass into the liquid. Of the molecules that strike the plane  $CD$  from below (that is, from the liquid side) only those will traverse the surface layer and pass through the plane  $AB$  into the vapor which have an upward velocity great enough to overcome the downward attraction exerted by the molecules within the surface layer. In other words, to escape from the liquid a molecule reaching the plane  $CD$  must have a velocity component  $x$  in the upward direction greater than a certain limiting value  $x_1$ , which value is equal to the decrease in upward velocity which any molecule would experience, in consequence of the molecular attraction, in passing from  $CD$  to  $AB$ . The fraction of the molecules that have an upward velocity component greater than this limiting value is given by the Maxwell distribution law (Art. 22); and from this fraction the number of such molecules reaching unit-area of the plane  $CD$  in unit time may be calculated, as shown in Prob. 10. The number of molecules that must be present in unit-volume of the vapor in order that there may impinge on unit-area of the plane  $AB$  in unit time a number of the molecules equal to that which escapes into the vapor is readily derived from the fundamental kinetic pressure hypothesis, as has already been indicated in Art. 18. It is evidently this number that determines the vapor-pressure of the liquid at any temperature.

The great effect of temperature on vapor-pressure is readily seen to be a consequence of these kinetic considerations. For it was shown in Art. 22 that the number of molecules which possess kinetic energies or velocities greater than any definite (relatively large) kinetic energy or velocity increases very rapidly with the temperature; thus this number at the two temperatures is represented in the figure of Art. 22 by the area lying beneath the two graphs, respectively, and to the right of an ordinate drawn at the definite value of the kinetic energy (for example, at the value  $K=2.0$ ).

The heat absorbed by the vaporization of a liquid at constant temperature is also accounted for by these considerations. For, when any molecule (of mass  $m$ ) passes from the liquid to the vapor, it evidently loses a quantity of kinetic energy equal to  $\frac{1}{2} m x_1^2$ ; and correspondingly, when one mol of liquid (containing  $\bar{n}$  molecules) vaporizes, the system loses a quantity of kinetic energy equal to  $\frac{1}{2} \bar{n} m x_1^2$ , consequently falls in temperature, and must absorb from the surroundings an equal quantity of heat (or other energy) if it is to return to its initial temperature. That is, the increase in energy-content

$\Delta U$  attending the vaporization of one mol of liquid at constant temperature, is given by the expression

$$\Delta \tilde{U} = \frac{1}{2} \bar{n} m x_1^2.$$

A striking result of these kinetic considerations is that they lead (as shown at the end of Prob. 10) to the Clapeyron equation, which was derived, entirely independently, from the laws of thermodynamics.

*\*Prob. 10. — Kinetic Expression for the Vapor-Pressure of a Liquid. —*

*a.* It can be shown with the aid of Maxwell's distribution law that, of all the molecules  $\bar{n}$  contained in one mol, the fraction  $dn/\bar{n}$  which have velocity-components along any one of the three rectangular axes with values between  $x$  and  $x + dx$  is given by the expression

$$\frac{dn}{\bar{n}} = \frac{0.69}{u} e^{-\frac{3x^2}{2u^2}} dx,$$

in which  $u$  denotes the square-root of the mean velocity-square. Formulate an expression for the number  $(dn/\bar{v}_L)$  of such molecules in unit-volume of the liquid, representing its molal volume by  $\bar{v}_L$ . *b.* Derive the following expression for the number  $dn_L$  of such molecules that strike unit-area of the plane  $CD$  in unit-time, noting that this number is equal to the number of them present in unit-volume multiplied by their upward velocity-component  $x$  and by a factor which represents the increase in the number of impacts on the plane resulting (as described in Art. 20) from the effect of the volume of the molecules, this factor being only a function of the molal volume of the liquid:

$$dn_L = 0.69 \frac{\bar{n}}{f(\bar{v}_L)} \frac{x}{u} e^{-\frac{3x^2}{2u^2}} dx.$$

*c.* By integrating this expression between the limits  $x_1$  and  $\infty$ , find an expression for the total number of molecules  $n_L$  striking the plane  $CD$  with a velocity-component greater than the critical one  $x_1$  (which barely permits their passage through the surface layer). *d.* By combining this result with the expression  $n_G = 0.23 u \bar{n} / \bar{v}_G$  (given in Art. 18) for the number of molecules  $n_G$  that strike in unit-time a unit-area of a plane bounding a perfect gas having one mol (and therefore  $\bar{n}$  molecules) in the volume  $\bar{v}_G$ , derive the following expression:

$$\frac{1}{\bar{v}_G} = \frac{1}{f(\bar{v}_L)} e^{-\frac{3x_1^2}{2u^2}}.$$

*e.* Derive for the vapor-pressure  $p$  the following expression, by replacing  $\bar{v}_G$  by the expression for it given by the perfect-gas equation:

$$p = \frac{RT}{f(\bar{v}_L)} e^{-\frac{3x_1^2}{2u^2}}.$$

*f.* By multiplying both numerator and denominator of the exponent of  $e$  by  $\bar{n}m$ , and noting that, as shown in the above text,  $\Delta \tilde{U} = \frac{1}{2} \bar{n} m x_1^2$ , and that, by Art. 19,  $\frac{1}{2} \bar{n} m u^2 = RT$ , derive the expression:

$$p = \frac{RT}{f(\bar{v}_L)} e^{-\frac{\Delta \tilde{U}}{RT}}.$$

g. Derive the approximate Clapeyron equation by differentiating the preceding equation with respect to  $T$  (regarding  $\tilde{v}_L$  as constant), dividing the resulting differential equation by the original one, and transforming; noting that the heat  $\Delta\tilde{H}$  absorbed by the vaporization of one mol of liquid at constant pressure and temperature is equal to the increase  $\Delta\tilde{U}$  in the energy-content of the system plus the work  $RT$  produced in the surroundings, that is, that  $\Delta\tilde{H} = \Delta\tilde{U} + RT$ .

## II. SOLUTIONS IN GENERAL

**35. The Nature and Composition of Solutions.** — A *solution* is a physically homogeneous mixture of two or more chemical substances; that is, one which has no larger aggregates than the molecules themselves. Solutions thus defined may be gaseous, liquid, or solid; but only liquid solutions will be here considered. When one substance is present in large proportion it is called the *solvent*, and any substance present in small proportion is called a *solute*.

In considering the equilibrium of solutions with the vapor or with the solid solvent, the term phase is conveniently employed. The *phases* of a system are its physically homogeneous parts, separated from one another by physical boundaries. Thus any gaseous mixture or any solution or any solid substance forms a single phase. A system may consist of any number of such phases. Thus a solution in contact with its vapor, or with the solid solvent, or with the solid solute, is an example of a two-phase system. A solution in contact both with the vapor and the solid solvent is a three-phase system.

The composition of solutions is often expressed in terms of the mol-fractions of the substances defined as in Art. 12. Thus, representing, as will be done throughout this chapter, quantities referring to the solvent by letters with the subscript zero, and those referring to the solute or solution by letters without subscripts, the *mol-fractions*  $x$  and  $x_0$  of the solute and solvent in a solution of two substances are defined by the equations  $x = N/(N_0 + N)$  and  $x_0 = N_0/(N_0 + N)$ , respectively. The proportion of solute may also be expressed in terms of the *mol-ratio*  $N/N_0$ . Composition is also expressed in terms of the number of formula-weights, of mols, or of equivalents, of solute in 1000 grams of solvent. Composition so expressed will be designated the *formality*  $f$ , the *molality*  $c$ , or the *weight-normality*  $c$ , respectively, of the solute in the solution. The term formality will be referred to the solute as a whole; but the terms molality and weight-normality will be used with reference to some definite chemical substance. Thus, a solution containing 0.1 formula-weight of  $\text{H}_2\text{SO}_3$  in 1000 g. of water is 0.1 formal (0.1 f.) in  $\text{H}_2\text{SO}_3$  (considered without reference to the chemical substances which it forms in solution); but, owing to partial ionization, this solution is 0.066 molal (0.066 m.) or 0.132 weight-normal (0.132 wn.) in  $\text{H}_2\text{SO}_3$ , and 0.034 molal or 0.034 weight-normal in  $\text{H}^+$  or in  $\text{HSO}_3^-$ . Composition will in this book be expressed in the terms of mol-fraction, mol-ratio, formality, molality,

or weight-normality, unless otherwise stated. Composition expressed in these ways has the advantage of being independent of temperature.

It is sometimes convenient, however, to employ true concentrations, which term strictly denotes the quantity of substance per unit-volume. The number of mols of solute per liter of solvent ( $N/v_0$ ) is called the *molal concentration*; and the solution is said to be  $x$  volume-molal in the solute. Thus a solution containing 0.1 mol of  $\text{NH}_3$  in one liter of chloroform at  $25^\circ$  is 0.1 volume-molal (0.1 vm.) in  $\text{NH}_3$  at  $25^\circ$ ; while it is 0.0675 (weight) molal (0.0675 m.) in  $\text{NH}_3$ , since 1000 g. of chloroform have a volume of 675 ccm. at  $25^\circ$ . In the case of aqueous solutions the molality and molal concentration evidently differ from each other in the same proportion that the density of water differs from unity; for example, by 0.3 percent at  $25^\circ$  and 4.3 percent at  $100^\circ$ . In connection with certain properties, such as the electrical conductance of solutions, which are directly related to the volume of the solution (not of the solvent), there will be employed the form of concentration familiar in volumetric analysis, called *normal concentration*, which is defined to be the number of equivalents of solute per liter of solution ( $N/v$ ). Thus an aqueous solution containing 1 equivalent of sulfuric acid in one liter of solution at  $25^\circ$  is 1 normal (1 n.) in  $\text{H}_2\text{SO}_4$  at  $25^\circ$ ; whereas this solution may be calculated with the aid of density data to be 1.020 weight-normal in  $\text{H}_2\text{SO}_4$  at any temperature.

With reference to the proportions in which the substances are present, two groups of solutions may be distinguished: *dilute solutions*, those in which the mol-fraction of the solute is small (not greater than 0.01 or 0.02); and *concentrated solutions*, those in which each substance is present in considerable proportion. There is, of course, no sharp line of demarcation between these two groups of solutions.

Some types of concentrated solutions and all dilute solutions conform approximately — more closely as the mol-fraction of the solute approaches zero — to certain laws, which, in analogy with the laws of perfect gases, may be called the *laws of perfect solutions*. The fundamental laws relating to the physical properties of perfect solutions are the vapor-pressure laws of Raoult and Henry, the corresponding laws of distribution between liquid phases, and the laws of the osmotic pressure of solutions. To consideration of these laws this chapter is mainly devoted.

### III. VAPOR-PRESSURE AND BOILING-POINT OF PERFECT SOLUTIONS WITH ONE VOLATILE COMPONENT

**36. Raoult's Law of Vapor-Pressure Lowering.** — *Raoult's law*, referred to above as one of the fundamental laws of perfect solutions, states that the addition of a <sup>Solute to a</sup> solvent causes at any temperature a fractional lowering of the vapor-pressure of the solvent equal to the mol-fraction ( $x$ ) of the solute. That is:

$$\frac{p_0 - p}{p_0} = \frac{N}{N_0 + N} = x,$$

where  $p_0$  is the vapor-pressure of the pure solvent and  $p$  is its vapor-pressure in a solution consisting of  $N$  mols of solute and  $N_0$  mols of solvent. In this expression  $N_0$  is equal to the weight  $m_0$  of the solvent divided by its molecular weight  $M_0$  in the *vapor*, and  $N$  is equal to the weight  $m$  of the solute divided by its molecular weight  $M$  in the *solution*. The value of  $M_0$  is ordinarily that corresponding to the molecular formula of the solvent; for, as stated in Art. 14, the molecular formula is commonly so written as to represent the molecular weight of the substance in the state of a perfect gas.

In the case of very dilute solutions the mol-fraction  $N/(N_0 + N)$  is evidently equal to the mol-ratio  $N/N_0$ ; and even in the case of moderately dilute solutions the mol-fraction may be replaced by the mol-ratio without causing appreciable error.

Although Raoult's law is exact only in the case of perfect solutions, it holds true approximately for all dilute solutions (usually within one or two percent up to a mol-fraction of 0.02), and for some concentrated solutions, as will be described in Art. 41.

The application of Raoult's law to solutions of moderate concentration affords an important method of determining the approximate molecular weight and the molecular composition of dissolved substances, as illustrated by the following problems.

*Determination of Molecular Weights and Molecular Composition.* —

**Prob. 11.** — At  $30^\circ$  the vapor-pressure of ethyl alcohol ( $C_2H_5OH$ ) is 78.0 mm., and that of an alcohol solution containing 5% of a non-volatile substance is 75.0 mm. What is the molecular weight of the substance?

**Prob. 12.** The experiment described in Prob. 2, Art. 31, was repeated, using in place of pure carbon bisulfide an 8.00% solution of sulfur in carbon bisulfide. 2.902 g. of carbon bisulfide were found to have vaporized. Calculate the molecular weight of the sulfur, and find its molecular formula.

Raoult's law may also be stated in the following simple form, which indicates more clearly its real significance: the vapor-pressure ( $p$ ) of the solvent in a perfect solution is proportional to its mol-fraction ( $x_0$ ); that is, representing by  $p_0$  the vapor-pressure of the pure solvent,

$$p = p_0 x_0.$$

*Prob. 13. — Mathematical Equivalence of the Two Forms of Raoult's Law.* — *a.* Show that the two statements of Raoult's law are mathematically equivalent. *b.* Show that the second statement of the law requires that the proportionality-factor be the vapor-pressure of the pure solvent, as is assumed in the mathematical expression of it.

Raoult's law relates fundamentally to the distribution between the liquid phase and vapor phase of the chemical substance whose partial pressure in the vapor is under consideration. In other words, from the molecular standpoint, it relates to the distribution of the kind of molecules which give rise to this partial pressure. It shows that the number of these molecules which are present in unit-volume of the vapor when equilibrium has been reached is proportional to the ratio in the liquid of the number of this kind of molecule to the total number of molecules of all kinds. Moreover, since this molecule-ratio is unity in the case of a solvent which consists solely of the kind of molecule under consideration, the proportionality-factor in this case is obviously the vapor-pressure of the pure solvent. It can be shown with the aid of the mass-action law that this is true also in the case that the solvent consists mainly of associated molecules (such as  $\text{H}_4\text{O}_2$ ) and contains only a small proportion of the simple molecules (such as  $\text{H}_2\text{O}$ ) of which the vapor consists.

When the vapor contains two or more kinds of molecules, owing to partial association of the simple solvent molecules or to the fact that the solute has an appreciable vapor-pressure, it is evident from these considerations that  $p$  and  $p_0$  in the Raoult equation denote, not the total vapor-pressures of the solution and solvent respectively, but the partial vapor-pressures due to the simple molecules.

\*The above-given forms of the Raoult equation also presuppose that the vapor conforms to the perfect-gas law. Fundamentally, Raoult's law expresses the tendency of the solvent to escape from the solution, and it should therefore be independent of the equation of state of the vapor. It can be shown by thermodynamic considerations that the simple Raoult equation can be corrected for the devia-

tion of the vapor from the perfect-gas law when this is expressed (as in Art. 15) by the equation  $p v = NRT (1 + \alpha p)$  by modifying it by the addition of another factor so that it assumes the following form, which will be called the *corrected Raoult equation*:

$$p = p_0 x_0 e^{\alpha(p_0 - p)} = p_0 x_0 [1 + \alpha(p_0 - p) + \frac{1}{2}\alpha^2(p_0 - p)^2 \dots].$$

**37. Relation of Boiling-Point Raising to Vapor-Pressure Lowering and Molal Composition.** — A relation between the increase in the boiling-point and the decrease in the vapor-pressure of a solvent produced by a non-volatile solute can be derived from the effect of temperature on the vapor-pressure of the solvent in the way shown in the following problems.

*Calculation of Boiling-Point Raising from Vapor-Pressure Lowering.* —

*Prob. 14.* — *a.* What is the vapor-pressure in mm. of a solution at  $100^\circ$  containing 5 g. of glucose ( $C_6H_{12}O_6$ ) in 100 g. of water? *b.* What is its boiling-point? Its vapor-pressure at  $100^\circ$ , like that of water, increases 3.58% per degree.

*Prob. 15.* — The vapor-pressure of ethyl alcohol is 721.5 mm. at  $77^\circ$ , 751.0 at  $78^\circ$ , 781.5 at  $79^\circ$ , and 813.0 at  $80^\circ$ . *a.* Plot on a large scale these vapor-pressures as ordinates and the temperatures as abscissas. Calculate the vapor-pressures at  $78^\circ$ ,  $79^\circ$ , and  $80^\circ$  of a solution consisting of 2 mols of a non-volatile solute and 98 mols of alcohol, and of one consisting of 4 mols of solute and 96 mols of alcohol; and plot these values on the diagram. *b.* With the aid of the diagram find the boiling-points at 1 atm. of pure alcohol and of the two solutions. *c.* Show from the geometrical relations of the diagram that the raising of the boiling-point is proportional to the lowering of the vapor-pressure at the boiling-point of the solvent, in the case of dilute solutions (for which the graphs may be considered to be parallel straight lines). *d.* Show from the geometrical relations that the ratio of the lowering of the vapor-pressure to the raising of the boiling-point, caused by adding the solute, is equal to the ratio of the increase in the vapor-pressure of the solvent caused by increasing the temperature to the increase in temperature, in the case of dilute solutions (for which the graphs may be considered straight lines).

Representing by  $T - T_0$  the raising of the boiling-point, and by  $p_0 - p$  the lowering of the vapor-pressure, produced by increasing the mol-fraction of the solute from 0 to  $x$ , and representing by  $\Delta p_0 / \Delta T_0$  the rate of change of the vapor-pressure of the solvent with the temperature, the relations derived in the preceding problem for dilute solutions may be expressed by the equation:

$$\frac{p_0 - p}{T_0 - T} = \frac{\Delta p_0}{\Delta T_0}; \text{ or } T - T_0 = \frac{\Delta T_0}{\Delta p_0 / p_0} \frac{p_0 - p}{p_0}. \quad (1)$$

The quantity  $\frac{\Delta T_0}{\Delta p_0/p_0}$  evidently corresponds to the quantity  $\frac{dT}{dp/p}$  in the approximate Clapeyron equation, and it is therefore equal to  $\frac{RT_0^2}{\Delta \tilde{H}_0}$ , where  $\Delta \tilde{H}_0$  denotes the molal heat of vaporization of the solvent at its boiling-point  $T_0$ . The relation between boiling-point raising and fractional vapor-pressure lowering is therefore also given approximately by the expression:

$$T - T_0 = \frac{RT_0^2}{\Delta \tilde{H}_0} \cdot \frac{p_0 - p}{p_0}. \quad (2)$$

By combining the expressions just derived with Raoult's equation for vapor-pressure lowering there may evidently be obtained the following relations between the raising of the boiling-point ( $T - T_0$ ) and the mol-fraction  $x$  of the solute:

$$T - T_0 = \left( \frac{dT_0}{dp_0/p_0} \right) x = \left( \frac{RT_0^2}{\Delta \tilde{H}_0} \right) x. \quad (3)$$

\*The preceding equations become exact only when infinitesimal changes in temperature, vapor-pressure, and mol-fraction are considered; for only in that case are the graphs in the diagram of Prob. 15 from which these equations were derived strictly parallel straight lines. It will be seen from the diagram that the following differential equation, corresponding to equation (1) above, holds true for any solution with a non-volatile solute having any mol-fraction  $x$ :

$$\left( \frac{\partial T}{\partial x} \right)_p = - \left( \frac{\partial T}{\partial p} \right)_x \left( \frac{\partial p}{\partial x} \right)_T. \quad (4)$$

\*From this equation there can be derived, as shown in Prob. 16, by substituting for the last two partial derivatives the expressions for them given by the Clapeyron equation (Art. 33) and the Raoult equation (Art. 36), the following equation:

$$dT = \frac{RT^2}{\Delta \tilde{H}} \frac{dx}{(1-x)}. \quad (5)$$

In this equation  $dT$  represents the raising in the boiling-point  $T$  caused by increasing the mol-fraction of the solute from  $x$  to  $x + dx$ , and  $\Delta \tilde{H}$  represents the heat absorbed in vaporizing one mol of solvent at the temperature  $T$  out of an infinite quantity of the solution (since it can be shown to have this significance when the Clapeyron equation is applied to vaporization out of a solution).

*\*Prob. 16. — Boiling-Point of Solutions Conforming to Raoult's Law at Any Concentration.* — *a.* State in words what each of the partial derivatives in equation (4) signifies. *b.* Find from the exact Clapeyron equation (neglecting the volume of the liquid) and from the corrected Raoult equation (given at the end of Art. 36) expressions for the last two of these partial derivatives, respectively. *c.* By substituting these expressions in the partial derivative equation, and simplifying it with the aid of the equation of state  $p\bar{v}=RT(1+\alpha p)$ , derive the expression for the boiling-point raising formulated as equation (5).

\*Equation (5) holds true even when the saturated vapor of the solvent does not conform to the perfect-gas law, as shown by its derivation. It can be integrated (as in Prob. 17), usually with negligible error, under the assumption that  $\Delta\tilde{H}$  does not vary with the temperature or with the mol-fraction of the solute, and that therefore it has the same value as the molal heat of vaporization  $\Delta\tilde{H}_0$  of the pure solvent at its boiling-point.

*\*Prob. 17. — Integration of the Boiling-Point Equation.* — *a.* Integrate equation (5) given in the text, assuming that the heat of vaporization does not vary with the temperature or the mol-fraction of the solute, so as to obtain a relation between the boiling-point of the solution, the boiling-point of the pure solvent, and the mol-fraction of the solute. *b.* Calculate the boiling-point of a solution consisting of 10 mols of a non-volatile solute and 90 mols of benzene. The heat of vaporization of one gram of benzene at its boiling-point  $80.3^\circ$  is 93.0 cal.

\*For small values of  $x$  and for the correspondingly small changes in the boiling-point  $T$  equation (5) may be integrated under the assumption that  $1-x$  is equal to unity and that  $T$  is constant and equal to  $T_0$ , and there then results equation (3), previously derived for dilute solutions, namely:

$$T - T_0 = \frac{RT_0^2}{\Delta\tilde{H}_0} x.$$

The quantity  $\frac{dT_0}{dp_0/p_0}$  or  $\frac{RT_0^2}{\Delta\tilde{H}_0}$  occurring in equation (3) is evidently a constant characteristic of the solvent. Representing this quantity, which may be called the *boiling-point constant*, by a single letter  $B_0$ , and noting that the mol-fraction  $x$  approaches the mol-ratio  $N/N_0$  as its value approaches zero, the law of boiling-point raising for perfect solutions may be expressed by the equation:

$$T - T_0 = B_0 \frac{N}{N_0}. \quad (6)$$

It is evident from this equation that the boiling-point constant  $B_0$  is the ratio of the boiling-point raising to the number of mols of solute which are associated with one mol of solvent; or, briefly, it is the boiling-point raising per mol of solute in one mol of solvent. It can be experimentally determined by measuring the rise in boiling-point produced by dissolving a definite weight of a solute of known molecular weight in a definite quantity of solvent. It can also, of course, be calculated from the change of vapor-pressure of the solvent with the temperature or from the molal heat of vaporization of the solvent by the above-given expressions. There are, accordingly, three kinds of data with the aid of which the boiling-point constant can be evaluated, as illustrated in Prob. 18.

In chemical literature is commonly recorded, not this boiling-point constant, but another constant, called the *molal boiling-point raising*, which is the boiling-point raising per mol of solute in 1000 grams of solvent. The value of this constant can obviously be readily calculated from that of the boiling-point constant (as in Prob. 19).

*Prob. 18. — Methods of Determining the Boiling-Point Constant.* — Calculate the boiling-point constant for ethyl alcohol from the following data. *a.* The heat of vaporization of one gram is 206 cal. at the boiling-point  $78.3^\circ$ . *b.* Its vapor-pressure has the values given in Prob. 15. *c.* The boiling-point of a solution of 1 g. of naphthalene ( $C_{10}H_8$ ) in 50 g. of alcohol is  $0.185^\circ$  higher than that of pure alcohol.

*Prob. 19. — Relation between the Boiling-Point Constant and the Molal Boiling-Point Raising.* — *a.* Calculate the molal boiling-point raising for water from its boiling-point constant. *b.* Formulate the algebraic relation between the two constants.

The following table contains the values of the constants for a few important solvents.

BOILING-POINT CONSTANTS				
	Water $H_2O$	Ethyl ether $C_4H_{10}O$	Ethyl alcohol $C_2H_5OH$	Benzene $C_6H_6$
Boiling-point constant . .	28.6	28.5	25.8	34.0
Molal boiling-point raising .	0.515	2.11	1.19	2.65

**38. Determination of Molecular Weights.** — From the value of either of the boiling-point constants for a given solvent there may be calculated by direct proportion the number of mols of solute corresponding to any observed raising of the boiling-point. The law of boiling-point raising, like Raoult's law from which it has been derived, therefore makes it possible to determine the molecular weights of substances in solution.

*Determination of Molecular Weight and Molecular Composition. —*

*Prob. 20. — a.* When 10.6 g. of a substance are dissolved in 740 g. of ether ( $C_4H_{10}O$ ), its boiling-point is raised  $0.284^\circ$ . What is the molecular weight of the substance? *b.* The substance is a hydrocarbon containing 90.50% of carbon. What is its molecular formula?

*Prob. 21. —* A solution of 3.04 g. of benzoic acid in 100 g. of ethyl alcohol boils  $0.288^\circ$  higher than pure alcohol. A solution of 6.34 g. of benzoic acid in 100 g. of benzene boils  $0.696^\circ$  higher than pure benzene. Calculate the molecular weight of benzoic acid in each of these solvents, and state what the results show in regard to its molecular formula in each solvent. Its composition by weight is expressed by  $C_6H_5CO_2H$ .

The molecular weights of substances are ordinarily found to be the same in the dissolved state as in the gaseous state; but hydroxyl compounds (such as the alcohols and organic acids) form in non-oxygenated solvents (such as benzene or chloroform) double or even more highly associated molecules. This indicates that the molecules of hydroxyl compounds are associated also in the state of pure liquids. Oxygenated solvents (such as water, alcohols, acetic acid, ether, and acetone) have the power of breaking down these associated molecules into the simple ones; and in such solvents nearly all organic substances have the same molecular weight as in the gaseous state.

**39. Partial Vapor-Pressure of Volatile Solutes. Henry's Law. —**

In addition to Raoult's law, which relates to the vapor-pressure of the solvent in a perfect solution, there is another fundamental law which relates to the vapor-pressure of the solute in such a solution. This law, known as *Henry's Law*, may be stated as follows. The partial vapor-pressure of any chemical substance present in small proportion in a solution is proportional to its mol-fraction. That is,

$$p = kx,$$

where  $k$  is a proportionality-constant dependent on the nature of the solute and of the solvent and on the temperature.

*Prob. 22. — Application of Henry's Law and Raoult's Law. —* The total vapor-pressure of a solution containing 3.00% by weight of ethyl alcohol ( $C_2H_5OH$ ) in water is 760 mm. at  $97.11^\circ$ , and the vapor-pressure of pure water at this temperature is 685 mm. Calculate with the help of Raoult's law and of Henry's law the vapor-pressures at  $97.11^\circ$  of ethyl alcohol and water in a solution containing 2.00 mol-percent of ethyl alcohol. *Ans.* 139 mm. for  $C_2H_5OH$ .

Henry's law may also be expressed in the following form, which makes it more obvious that it is a law of equilibrium which determines the distribution of the solute between the solution and a gaseous

phase, and which incidentally expresses the composition of the solution in terms either of molality or of molal concentration (defined as in Art. 35), instead of as mol-fraction. Any chemical substance present as a perfect gas in a vapor phase and as a solute in a perfect solution in equilibrium with it has at any definite temperature a molality or molal concentration  $c$  in the solution which is proportional to its (partial) pressure  $p$  in the gaseous phase. That is,

$$c/p = K,$$

where  $K$  is an equilibrium-constant which is determined by the nature of the chemical substance and of the solvent and by the temperature. The equilibrium concentration  $c$  is the *solubility* of the substance when its partial pressure in the gas phase is  $p$ , and the equilibrium-constant  $K$  may be called the *solubility-constant* of the gaseous substance in the solvent. Henry's law is therefore a law of the solubility of gases.

This second form of Henry's law is for perfect solutions equivalent to the first form. For, on the one hand, the mol-fraction  $N/N_0 + N$ , as it approaches zero, becomes equal to the mol-ratio  $N/N_0$ , and this is evidently proportional to the molality ( $1000N/m_0$ ) or to the molal concentration ( $N/v_0$ ); and, on the other hand, the vapor-pressure of a substance in a solution is equal to its partial pressure in a gaseous phase that is in equilibrium with the solution.

Henry's law in either of its two forms is conformed to more closely as the pressure of the gas and the concentration of the solute approach zero. Like the other laws of perfect solutions, it usually holds true within 2 to 3 percent, even when the pressure is one atmosphere and the concentration 1 molal.

It is to be noted that Henry's law expresses conditions of equilibrium, and that these conditions are often attained between a gaseous and liquid phase only by long-continued intimate contact.

From a molecular standpoint, Henry's law, like Raoult's law, relates to the distribution of some definite kind of molecule between the gas phase and the liquid phase. Hence in applications of it the same chemical substance in the two phases must be considered. Thus, when the chemical substance  $\text{SO}_2$  dissolves in water it is largely converted into  $\text{H}_2\text{SO}_3$  and its ions  $\text{H}^+$  and  $\text{HSO}_3^-$ ; and Henry's law therefore requires, not that the total concentration of solute in the solution, but that the concentration of the  $\text{SO}_2$  itself, be proportional to the partial pressure of the  $\text{SO}_2$  in the vapor. When, however, the only change in

the substance is that it partially combines with the solvent forming a *solvate* (a *hydrate* in the case of water), then the total concentration may be employed; for the fraction solvated is in dilute solution independent of the concentration of the substance, as may be shown by the mass-action law. Thus, though the substance  $\text{CO}_2$  on dissolving in water is partly converted into the hydrate  $\text{H}_2\text{CO}_3$  (which is substantially unionized, except at very small concentrations), yet the solubility of carbon dioxide gas, as found by determining the total quantity dissolved, changes with the pressure in accordance with Henry's law.

These considerations also show that in applying Henry's law the partial pressure of the chemical substance in the gas phase, not the total pressure of the gas, must be considered. Thus the quantity of carbon dioxide dissolved by water in contact with air is not determined by the pressure of the air, but by the partial pressure of  $\text{CO}_2$  in the air.

*Prob. 23. — Determination of the Vapor-Pressure of Solutes.* — A mixture of air and ammonia containing 1 mol-percent of  $\text{NH}_3$  is passed at  $25^\circ$  and 1 atm. through water. The saturated solution is found by titration to be 0.553 formal in  $\text{NH}_4\text{OH}$ . Calculate the partial vapor-pressure of  $\text{NH}_3$  in a 1 formal solution at  $25^\circ$ . The vapor-pressure of water at  $25^\circ$  is 23.8 mm.

*Solubility of Gases in Water.* —

*Prob. 24.* — In a gas buret over mercury 60 ccm. of dry carbon dioxide at  $25^\circ$  and 1 atm. are placed, 40 ccm. of water are introduced, and the gas and water are shaken together at  $25^\circ$  till equilibrium is reached, keeping the pressure on the gas 1 atm. The volume of the (moist) gas is then found to be 28.9 ccm. Calculate the molal solubility of carbon dioxide in water at  $25^\circ$  when its partial pressure is 1 atm., neglecting effects that influence the result less than 0.5%. *Ans.* 0.0338.

*Prob. 25.* At  $20^\circ$  100 g. of water dissolve 3.4 ccm. of oxygen, 1.7 ccm. of nitrogen, and 3.8 ccm. of argon when the pressure of each gas is 1 atm. *a.* Calculate the corresponding molal solubility of each gas. *b.* Calculate the mol-fraction of each constituent in the gas-mixture obtained by shaking water at  $20^\circ$  with air (free from  $\text{CO}_2$ ), expelling the dissolved gas by boiling and drying it. Tabulate the molal composition of this gas with that of air (given in Art. 12). *Ans. b,* 0.34 for  $\text{O}_2$ .

*Prob. 26. — Determination of the State of Substances in Solution.* — The partial vapor-pressure of  $\text{NH}_3$  in an aqueous solution 0.3 formal in  $\text{NH}_3$  and 0.1 formal in  $\text{AgNO}_3$  is at  $25^\circ$  equal to that in a 0.1 formal solution of  $\text{NH}_3$  in water. State and explain the conclusion that can be drawn as to the formula of the complex salt formed, considering all the silver nitrate to be combined with ammonia, and assuming that the solubility-constant of the  $\text{NH}_3$  is not affected by the silver salt.

Aside from any chemical action, the addition to the water of a salt commonly decreases the solubility of a volatile substance at a given pressure in the gas phase; or conversely, it increases its vapor-pressure at a given concentration in the solution. This phenomenon, which is known as the *salting-out effect*, is subject to the following principles:

(1) The decrease of the solubility-constant is approximately proportional to the concentration of the added salt, up to concentrations not much exceeding 1 normal.

(2) The fractional decrease per equivalent of salt per 1000 grams of water is roughly the same for a definite salt, whatever be the nature of the solute.

(3) This fractional decrease varies greatly with the nature of the salt; thus the decrease caused by 0.1 equivalent of salt per 1000 grams of water varies from about zero in the case of barium nitrate to about 4 percent in the case of potassium and sodium sulfates.

*Prob. 27. — The Salting-out Effect.* — The solubility (that is, the concentration of the saturated solution) of carbon dioxide at  $25^{\circ}$  and 1 atm. is 0.0338 molal in pure water and 0.0331 in a 1 normal NaCl solution. The vapor-pressure of ammonia from a 0.5 molal solution of it in water at  $25^{\circ}$  is 6.65 mm. Predict from the principles of the salting-out effect the ammonia vapor-pressure for a solution 0.5 molal in  $\text{NH}_3$  and 0.5 normal in NaCl.

#### IV. VAPOR-PRESSURE AND BOILING-POINT OF CONCENTRATED SOLUTIONS WITH TWO VOLATILE COMPONENTS

**40. The Vapor-Pressure of Concentrated Solutions.**—Concentrated solutions may be divided for purposes of consideration into two groups as follows. One group consists of those solutions whose formation out of their pure components (when these are liquid) is not attended by any considerable change of temperature or volume, and whose properties in general are approximately the sum or average of those of the pure components. The characteristic of such solutions is that neither component exerts a specific influence on the properties of the other component. Such solutions conform approximately — more closely as the condition characterizing them is more nearly fulfilled — to the laws of perfect solutions. Concentrated solutions which are considered to conform to these laws may be called *concentrated perfect solutions*. The other group of concentrated solutions consists of those whose components exert a marked influence upon one another. For these solutions no general laws are known.

The method commonly employed for experimentally determining at any definite temperature the partial vapor-pressures of solutions consisting of two or more volatile components is to distil off a small fraction from a large volume of the solution, adjusting the pressure on the liquid so that it boils at this temperature. The composition of the distillate is then determined by chemical analysis or by the measurement of some physical property, such as density; and from this composition and the pressure under which the distillation took place the partial vapor-pressures are calculated by Dalton's law.

*Prob. 28.—Experimental Determination of Partial Vapor-Pressures.*—A solution of two substances A and B containing  $N_A$  mols of A and  $N_B$  mols of B boils at the temperature  $T$  when a pressure  $p$  is exerted upon it. The first portion of distillate consists of  $N_A'$  mols of A and  $N_B'$  mols of B. Derive an algebraic expression for the partial vapor-pressures  $p_A$  and  $p_B$  of the two substances in the solution, explaining the principles involved.

**41. Vapor-Pressure and Boiling-Point of Concentrated Perfect Solutions in Relation to their Molal Composition.**—In concentrated perfect solutions the vapor-pressure of each component conforms approximately to Raoult's law. In other words, the partial vapor-pressure of each component is approximately equal to the product of its mol-fraction in the solution by its vapor-pressure in the pure state, whatever be the proportion in which the components are present; that is,  $p_A = p_{0A} x_A$ ,  $p_B = p_{0B} x_B, \dots$

*Prob. 29. — Vapor-Pressure-Composition Diagram for Perfect Solutions. —* At 50° the partial vapor-pressures of benzene and of ethylene chloride in solutions of these two substances have been found experimentally to have the following values:

Mol-fraction of $C_6H_6$	Vapor-pressure of $C_6H_6$	Vapor-pressure of $C_2H_4Cl_2$
1.000	268 mm.	0 mm
0.707	190	68
0.478	128	123
0.246	66	178
0.000	0	236

*a.* Plot on a large scale these partial vapor-pressures, and the corresponding total vapor-pressures, as ordinates against the mol-fractions as abscissas. Show that the three graphs are in almost complete accord with Raoult's law. *b.* Calculate the mol-fraction of benzene in the vapor which at 50° is in equilibrium with each of the three solutions for which the data are given in the above table. *c.* On a new larger-scale vapor-pressure-composition diagram (with ordinates covering only the interval of 230–270 mm.) draw a line showing the variation of the total vapor-pressure with the mol-fraction of the liquid mixture. Plot also on this diagram the compositions of the vapor calculated in *b* against the total vapor-pressures, considering that the abscissas now represent the mol-fraction of benzene in the vapor.

*Prob. 30. — Distillation at Constant Temperature of Perfect Solutions. —* At 50° a small fraction is distilled off from a large volume of a solution containing equimolal quantities of benzene and ethylene chloride, and this distillate is redistilled at 50°. Derive from the diagram of Prob. 29 the mol-fraction of benzene in the first part of the second distillate. *Ans.* 0.56.

\*The boiling-point of a solution that contains two volatile components whose partial vapor-pressures both conform to Raoult's law can best be derived graphically from the vapor-pressures of the pure substances, as illustrated by the following problem.

*\*Prob. 31. — Boiling-Point-Composition Diagram for Perfect Solutions.*  
The vapor pressure at . . . . 80°, 83°, 86°, 89°, 92°  
of a pure liquid A is . . . . 560, 610, 665, 725, 790 mm.  
and of a pure liquid B is . . . . 400, 435, 475, 520, 570 mm.

*a.* With the aid of these data and Raoult's law, draw on a large-scale vapor-pressure-composition diagram for each temperature two lines — one representing the total vapor-pressure of any solution of A and B; and the other representing the partial vapor-pressure of A above any solution. *b.* Determine from the plot the composition of the liquid which at 570 mm. boils at each of these temperatures; also the composition of the vapor which is in equilibrium with each of these solutions at

its boiling-point. Determine also the boiling-point of the pure liquid A at 570 mm., and tabulate all of these results. *c.* On another large-scale diagram plot against these liquid-compositions the boiling-points as ordinates. Plot also the vapor-compositions against the corresponding boiling-points.

*Distillation at Constant Pressure of Perfect Solutions. —*

*\*Prob. 32.* — A solution of 100 mols of each of the liquids of Prob. 31 is distilled at 570 mm. until its boiling-point rises  $0.5^{\circ}$ . *a.* Find from the diagram of Prob. 31*c* the molal compositions of the first and last portions of the distillate. *b.* Regarding the composition of the whole distillate as the mean of that of its first and last portions (which is approximately true when only a small fraction of the liquid distills over), calculate the number of mols of A and of B in the distillate and in the residue. *c.* The distillation of the residue is continued till its boiling-point rises  $0.5^{\circ}$  more. Calculate as in *b* the number of mols of A and B in this second distillate and in the residue. *d.* Tabulate the number of mols of A and B in the original liquid, the first distillate, the second distillate, and the final residue; the mol-fraction of A in each of these liquids; and the boiling-point of each of them. *Ans. b,* 52 mols of A, and 63 mols of B in the residue.

*\*Prob. 33.* *a.* The first distillate obtained in Prob. 32*a* is redistilled until the residue attains the composition of the second distillate obtained in Prob. 32*c*. Find the mol-fraction of A in the new distillate and its boiling-point. *b.* The residue is now mixed with the second distillate obtained in Prob. 32*c*, and the distillation is continued till the residue has the composition of the residue obtained in Prob. 32*c*. Find the mol-fraction of A in the distillate thus obtained and its boiling-point. *c.* Tabulate the composition and the boiling-point of the original equimolal solution and of the three fractions into which it has now been resolved. *Ans. b,* mol-fraction, 0.55; boiling-point,  $85.5^{\circ}$ .

The foregoing considerations show that any perfect solution submitted to distillation resolves itself into a distillate containing a larger proportion, and into a residue containing a smaller proportion, of the more volatile component. It is evident that, in consequence of this behavior, the two components can be completely separated from each other by repeated fractional distillation, carried out as illustrated by Probs. 32 and 33.

**42. Vapor-Pressure of Concentrated Solutions in General in Relation to their Composition.** — There are comparatively few actual solutions which fulfil strictly the criterion stated in Art. 40 of being formed out of their components without any change of temperature or volume; and correspondingly, comparatively few concentrated

solutions conform completely to Raoult's law of perfect solutions. The law is therefore to be regarded as a limiting law, from which actual solutions deviate to an extent which is as a rule roughly indicated by the magnitude of the changes of temperature and volume attending the mixing of the components.

The data given below illustrate the magnitude of the deviations from the law for a variety of solutions. The first two columns of figures show the change of temperature and the percentage change of volume which result when equimolal quantities of the two substances at the same temperature are mixed. The last three columns show the percentage difference between the observed values of the partial (or total) vapor-pressures of the equimolal solution and those calculated by Raoult's law; namely, the values of the vapor-pressure ratio  $100(p_{\text{obs.}} - p_{\text{calc.}})/p_{\text{calc.}}$ .

#### DEVIATIONS FROM RAOULT'S LAW

Mixture No.	Components		Change of Temperature	Change of Volume	Percentage Deviation of Pressure		
	A	B			A	B	A+B
1	C <sub>6</sub> H <sub>5</sub> Cl	C <sub>6</sub> H <sub>5</sub> Br	0.0°	0.0%	- 0.1	- 0.1	-
2	C <sub>6</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub> Cl <sub>2</sub>	- 0.3	+ 0.34	+ 0.1	- 0.2	-
3	CHCl <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CO	+ 12.4	- 0.23	- 23.	- 18.	-
4	CS <sub>2</sub>	CH <sub>2</sub> (OCH <sub>3</sub> ) <sub>2</sub>	- 6.5	+ 1.22	+ 10.	+ 7.	-
5	CS <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> CO	- 9.8	+ 1.21	+ 40.	+ 58.	-
6	C <sub>6</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>5</sub> OH	- 4.2	0.0	-	-	+ 50

The character of the deviations from Raoult's law can be best appreciated by considering their causes from molecular and kinetic view-points. It has already been seen (in Art. 34) that the vapor-pressure of a solvent is determined primarily by the proportion of its molecules which at any temperature acquire an outward velocity sufficient to overcome the inward attraction of the other molecules and thus escape through the surface layer into the gas phase. Consider now the different conditions that may result when another substance B is added to the solvent A.

(1) In case the B molecules exert upon the A molecules the same attraction as the A molecules exert on one another, the attraction upon the A molecules in the mixture, and hence their escaping velocity, will be the same as in the pure solvent, the proportion of them that acquire this escaping velocity will be the same, and the absolute number of them which escape will be diminished only in the proportion in which the proportion of A molecules in the liquid is reduced. In this case, therefore, the vapor-pressure of A will be directly propor-

tional to its mol-fraction, as Raoult's law requires; and little if any heat-effect or volume change will take place on mixing the components.

(2) In case the B molecules exert upon the A molecules a smaller attraction than they exert upon one another, the escaping velocity will be smaller and the proportion of the A molecules that acquire this velocity will be greater in the solution than in the pure solvent; and correspondingly the vapor-pressure of A will be greater than Raoult's law requires. In this case the mixing of the two components will be attended by an increase in volume and a fall in temperature (due to the expansion and attendant separation of the molecules in opposition to their attraction).

(3) In case the B molecules exert upon the A molecules a greater attraction than the latter exert on one another, the opposite effects to those just considered will evidently result.

(4) In case the B molecules form with the A molecules a chemical compound (such as AB,  $A_2B$ , or  $AB_2$ ), the fraction of A molecules in the liquid is decreased, not only as always by the presence of the new molecules, but in this case also by the conversion of some of the A molecules into those of the compound. This will evidently result in a smaller vapor-pressure than Raoult's law requires. In this case an evolution of heat and diminution of volume may be expected, since the synthetic formation of chemical compounds is usually attended by these effects.

(5) In case the simple molecules A of the solvent are partially associated, to form double or more complex molecules, such as  $A_2$  or  $A_3$ , some of the latter will be dissociated, in accordance with the mass-action law, when the solvent is diluted by the addition of the substance B, and the partial pressure of the simple A molecules in the vapor will be correspondingly increased. In this case, a fall in temperature may be expected, since dissociation is commonly attended by absorption of heat.

The foregoing considerations are not of a quantitative character; and on the chemical effects described in (4) and (5) may be superposed the physical effects mentioned in (2) and (3). These molecular considerations, however, often assist in interpreting the vapor-pressure of mixtures.

*Prob. 34. — Molecular Explanations of the Deviations from Raoult's Law.* — Suggest the most probable molecular explanation of the behavior of each of the mixtures for which data are given in the above table, taking into account all the foregoing considerations.

*Prob. 35. — Compound Formation Derived from the Vapor-Pressure Relations.* — At  $35.2^\circ$  the vapor-pressure of acetone,  $(\text{CH}_3)_2\text{CO}$ , is 345 mm. and that of chloroform,  $\text{CHCl}_3$ , is 293 mm. In a 50 mol-percent mixture of these substances the vapor-pressure of the acetone is 141 mm. and that of the chloroform is 113 mm. Assuming that the apparent deviation from Raoult's law is wholly due to the formation of a non-volatile compound  $(\text{CH}_3)_2\text{CO} \cdot \text{CHCl}_3$ , calculate the mol-percent of this compound and the mol-percents of uncombined  $(\text{CH}_3)_2\text{CO}$  and  $\text{CHCl}_3$ , *a*, from the vapor-pressures of the acetone; and *b*, from those of the chloroform. *Ans.*  $(\text{CH}_3)_2\text{CO} \cdot \text{CHCl}_3$ : *a*, 18.2, *b*, 22.8.

In connection with the deviations from Raoult's law it should be borne in mind that, as the mol-fraction of any component approaches unity, so that the solution becomes dilute with respect to the other component, its partial vapor-pressure always approaches that required by Raoult's law, and the partial vapor-pressure of the other component conforms to Henry's law, however great the deviation may be when both components are present in large proportion.

Vapor-pressure-composition diagrams for solutions whose components do not conform to Raoult's law can be constructed only with the aid of experimentally determined data. By reference to such diagrams the behavior of the solutions when submitted to distillation at constant temperature can be predicted.

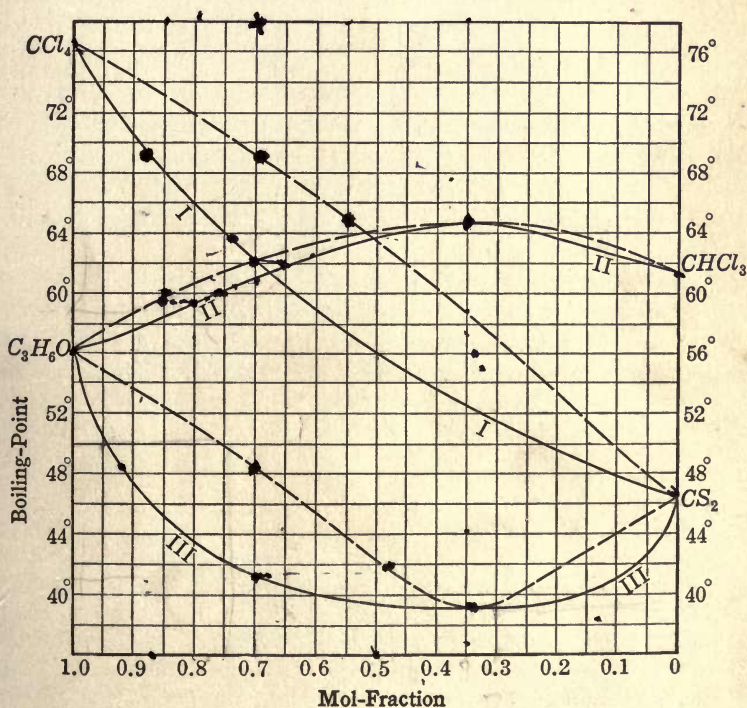
*Prob. 36. — Construction of Vapor-Pressure-Composition Diagrams.* — *a.* Draw on a large-scale diagram vapor-pressure curves representing the partial vapor-pressure at  $35.2^\circ$  of carbon bisulfide and of acetone in solutions of these components throughout the whole range of composition. Assume that Raoult's law and Henry's law hold with this pair of components up to 5 mol-percent; and make use of the following values in millimeters of the vapor-pressures at  $35.2^\circ$ :

Mol-percent of $\text{CS}_2$	0	1	20	40	60	80	99	100
Vapor-pressure of $\text{CS}_2$	0	17.8	274	377	425	460	—	518
Vapor-pressure of $(\text{CH}_3)_2\text{CO}$	353	—	289	255	228	187	20.1	0

*b.* On the same diagram draw a curve representing the total vapor-pressures of the solutions. Draw on the diagram dotted lines showing what the partial and total vapor-pressures would be if the solutions behaved as perfect solutions. *c.* Calculate the mol-percents of  $\text{CS}_2$  in the vapor in equilibrium with the 5, 20, 40, 60, 80, and 95 mol-percent liquid solutions; and on the same diagram plot these vapor-compositions against the total pressures and draw a dotted line through the points.

**43. Boiling-Point of Concentrated Solutions in General in Relation to their Composition.** — The boiling-point-composition diagrams for solutions whose vapor-pressures do not conform to Raoult's law can be based upon direct experimental determinations of the boiling-point

of solutions of known composition and upon analyses of the corresponding distillates. All that can be done, in the way of generalization, is to consider the different types of curves to which different pairs of substances conform. The figure shows the three types of curves exhibited by substances miscible in all proportions. In each case the solid curve shows the compositions (expressed as mol-fractions) and corresponding boiling-points of the liquid solutions at one atmosphere; and the broken curve shows the composition of the vapor that is in equilibrium with these solutions. Thus any point on a broken curve represents the composition of the vapor of the liquid solution whose point lies in the same horizontal line.



Curve I is the experimentally determined curve for solutions of carbon tetrachloride (b. pt., 76.7°) and carbon bisulfide (b. pt., 46.3°). Curve II is that for solutions of acetone (b. pt., 56.2°) and chloroform (b. pt., 61.3°). Curve III is that for solutions of acetone (b. pt., 56.2°) and carbon bisulfide (b. pt., 46.3°).

Solutions of type I, when subjected to fractional distillation, behave like perfect solutions (which form a special case of this type), and may like them be finally resolved into the pure components. The behavior of solutions of types II and III on fractional distillation is shown in the following problems.

*Fractional Distillation of Solutions. —*

*Prob. 37. — a.* Determine from curve III in the figure the boiling-point and composition of the first portion of distillate obtained by distillation of solutions of acetone and carbon bisulfide containing 70 mol-percent of acetone, 15 mol-percent of acetone, and 35 mol-percent of acetone, respectively. Tabulate the boiling-point and composition of each solution and distillate. *b.* State in what respects each distillate and each residue differs from the solution from which it was obtained. *c.* If each of the solutions were submitted repeatedly to fractional distillation, what would be the composition of the products finally obtained as distillate and as residue? *d.* If of the 70 mol-percent solution 1000 g. were so fractionated, what weight of each product would be obtained? *Ans. d,* 508 g. of distillate, 492 g. of residue. •

*Prob. 38. —* By reference to curve II in the figure answer the same questions for solutions of acetone and chloroform as are asked in Prob. 37*a*, 37*b*, and 37*c*, for solutions of acetone and carbon bisulfide.

Just as the solid lines in such temperature-composition diagrams show the boiling-points of any liquid solution, so the broken lines show the condensation-point at one atmosphere of vapor of any composition; the composition of the liquid which first condenses out of it being given by the corresponding point on the solid line. Such diagrams therefore serve to predict the behavior of vapors when subjected to fractional condensation, as illustrated by the following problem.

The processes used in chemical practice for the separation of volatile liquids, such as alcohol and water or benzene and toluene, involve fractional distillations and condensations taking place in accordance with the principles here considered.

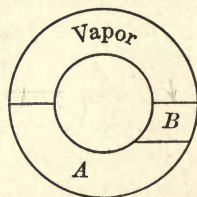
*Prob. 39. — Fractional Condensation of Vapors. — a.* A vapor composed of equimolal quantities of carbon tetrachloride and carbon bisulfide is cooled at 1 atm. till condensation begins. By referring to curve I in the figure find the temperature at which condensation begins, and the composition of the condensate. *b.* The vapor is gradually cooled, removing the condensate as it forms, till the temperature falls to 60°. Find the composition of the condensate which is now separating, and that of the residual vapor. *c.* Tabulate the composition (50 mol-percent) of the original vapor, the average composition of

the condensate obtained from it in *b*, and the composition of the residual vapor. Include in the table also the composition of the liquid which upon distillation would furnish the original vapor.

## V. DISTRIBUTION BETWEEN PARTIALLY MISCIBLE SOLVENTS

**44. Determination of Equilibrium-Conditions by the Perpetual-Motion Principle.** — Before considering other molal properties of solutions it is desirable to present an energy principle which is of great value in predicting the equilibrium conditions of systems consisting of two or more phases. This principle is illustrated by Prob. 40 and discussed in the succeeding paragraph.

*Prob. 40. — Condition of Equilibrium between Two Phases.* — A volatile substance S is dissolved in each of two non-miscible solvents, the two solutions A and B being shaken together at some definite temperature till equilibrium is reached. They are placed, as in the figure, in contact with the vapor-phase containing the substance S at a pressure equal to its partial vapor-pressure in solution A. Show that if this pressure were greater or less than the partial vapor-pressure of S in the solution B, the substance S would pass continuously through the three phases of the system under a difference of pressure, whereby work could be produced.



*Perpetual motion* (of the kind here considered) signifies in general an ideal process by which an unlimited amount of work might be produced by a system operating in surroundings of constant temperature and drawing from them no work. Thus, in the case considered in Prob. 40, if the vapor-pressures of the substance in the two solutions were different, a current of its vapor would flow continuously from one surface to the other, and work could be obtained from the moving vapor for an unlimited period of time, for example, by placing a wind-mill in the vapor-space. Even though a quantity of heat equivalent to the work produced were taken up from the surroundings, the process would still be a kind of perpetual motion which is impossible, as will be seen later in the discussion of the second law of thermodynamics.

The principle that perpetual motion of this kind is impossible is often employed, as in this instance, for determining the conditions of equilibrium between the different phases of a system. It leads in such cases to the general conclusion that, if two phases are each in equilibrium with a third phase, they must be in equilibrium with each other, with respect to every substance that is present. This principle will hereafter be called simply the *perpetual-motion principle*.

**45. Distribution of a Solute between Two Non-Miscible Solvents.** — There has been experimentally established another important law

of perfect solutions, as follows. At any definite temperature the ratio between the equilibrium concentrations  $c_A$  and  $c_B$  of a chemical substance S in two non-miscible solvents (A and B) is constant, whatever be the initial concentrations. That is

$$c_A/c_B = K,$$

where  $K$  is a constant, called the *distribution-ratio*, determined by the nature of the substances A, B, and S, and by the temperature.

This law may be generalized so as to be applicable to the distribution of a definite chemical substance between any two kinds of phases. Thus in its general form it includes Henry's law, since the pressure of a gas at any definite temperature is proportional to its concentration; that is, since  $p = (N/v)RT = cRT$ . It is called the law of distribution between phases, or simply the *distribution law*.

This distribution law, like Raoult's law and Henry's law, is a limiting law which becomes more exact as the concentrations approach zero, but which holds true approximately up to moderate concentrations such as 1 molal.

The distribution-ratio of a solute between water and another solvent is decreased by the addition of a salt to the water in accordance with the principles of the salting-out effect stated in Art. 39.

The distribution law between liquid phases can be derived from Henry's law and the perpetual-motion principle (as in Prob. 41) for a volatile solute. This derivation is general, since every solute has a vapor-pressure, even though it may be too small to measure.

In considering the distribution of solutes between liquid phases, the concentration is usually expressed in mols per 1000 ccm. of solvent, instead of in mols per 1000 grams of solvent; and the value of the distribution-ratio varies correspondingly. In the problems of this article such volume concentrations are employed.

*Prob. 41. — Derivation of the Distribution Law.* — Derive the law of the distribution of a volatile solute between two solvents from Henry's law and the conclusion reached in Prob. 40.

*Prob. 42. — Evaluation of the Distribution-Ratio from Vapor-Pressure Data.* — At 25° the vapor-pressure of ammonia above a 0.1 volume-molal (vm.) solution of it in chloroform is 33.25 mm., and above a 0.5 vm. solution of it in water is 6.65 mm. *a.* What is the distribution-ratio of ammonia between water and chloroform? *b.* What would be its distribution-ratio between a 0.5 n. NaCl solution and chloroform?

*Prob. 43. — Extraction of Solutes from Aqueous Solutions by Organic Solvents.* — The distribution-ratio of an organic acid between water and

ether at  $20^{\circ}$  is 0.4. A solution of 5 g. of the acid in 100 ccm. of water is shaken successively with three 20-ccm. portions of ether. *a.* How much acid is left in the water? *b.* How much acid would have been left in the water if the solution had been shaken once with a 60-ccm. portion of ether? *Ans.* *a.* 1.48; *b.* 2.00.

*Prob. 44. — Determination of Complex Salt Formation.* — An aqueous solution containing 0.25 KCl and 0.20  $\text{HgCl}_2$  in one liter of water is shaken with an equal volume of benzene at  $25^{\circ}$ . The benzene phase is found by analysis to contain 0.0057 mol of  $\text{HgCl}_2$  per liter, but no KCl. The distribution-ratio of  $\text{HgCl}_2$  between water and benzene at  $25^{\circ}$  is 13.3. *a.* Calculate the total concentration of mercuric chloride in the aqueous phase and the concentration of the part of it which is combined with the potassium chloride (neglecting the salting-out effect). *b.* The complex salt has been shown by other measurements to be  $\text{KHgCl}_3$ . Tabulate its concentration and the concentrations of the (uncombined) KCl and  $\text{HgCl}_2$ . *Ans.* 0.1185  $\text{KHgCl}_3$  per liter.

**\*46. The Lowering by Solutes of the Solubility of One Solvent in Another Solvent.** — The solubility of one solvent, such as water, in another solvent, such as ether, is found to be lowered by dissolving in the first solvent a solute, such as sodium chloride. The general law expressing this effect corresponds in form to Raoult's law of vapor-pressure lowering. This law, called the *law of solubility lowering*, may be stated as follows. If in a solvent A, which has a small solubility  $s_0$  in another solvent B, there is dissolved a solute S (not soluble in the solvent B) whose mol-fraction in A has any small value  $x$ , the solubility  $s$  of A in B is now less than its original value  $s_0$  to the extent required by the law that the fractional lowering of solubility is equal to the mol-fraction of the solute. That is:

$$\frac{s_0 - s}{s_0} = x.$$

The law of solubility lowering can be derived from Raoult's law, Henry's law, and the perpetual motion principle, as shown in the following problem.

*Prob. 45. — Derivation of the Law of Solubility Lowering.* — Show how the law of solubility lowering can be derived from Raoult's law of vapor-pressure lowering with the aid of the perpetual-motion principle (applied to the vapor of the substance A above the two liquid phases) and of Henry's law (applied to the equilibrium of the substance A between the vapor phase and the solution of A in B).

*Prob. 46. — Application of the Law of Solubility Lowering.* — The solubility of isoamyl alcohol ( $\text{C}_5\text{H}_{11}\text{OH}$ ) in water at  $25^{\circ}$  is 0.280 mol per 1000 g. Calculate its solubility in water when 0.5 mol of chloroform ( $\text{CHCl}_3$ ) is dissolved in 1000 g. of isoamyl alcohol.

**47. The Vapor-Pressure Relations of Partially Miscible Liquids.** — Raoult's law, Henry's law, and the perpetual-motion principle make it possible to predict in part the vapor-pressure relations of liquids which have limited solubilities in each other, as is illustrated in Prob. 47.

*Prob. 47. — The Vapor-Pressure-Composition Diagram for Partially Miscible Liquids.* — When isoamyl alcohol ( $C_5H_{11}OH$ ) and water are shaken together at  $25^\circ$  till equilibrium is attained, two liquid phases result, one containing 36.84 mol-percent, and the other 99.50 mol-percent of water. *a.* Calculate the vapor-pressure of the water in each of the phases from the vapor-pressure, 23.8 mm., of pure water at  $25^\circ$ , regarding the isoamyl alcohol present in small proportion in the aqueous phase as a perfect solute. *b.* Construct a diagram showing the vapor-pressure of water in all mixtures of these two substances at  $25^\circ$ , with the aid of the above values and the following data. The vapor-pressure of water at  $25^\circ$  is 19.1 mm. in a 20.5 mol-percent, 14.5 mm. in 13.1 mol-percent, and 8.4 mm. in a 6.9 mol-percent solution of it in isoamyl alcohol. Note that the water must conform to Henry's law so long as it is present at small concentration.

*Prob. 48. — Steam Distillation of Liquids Partially Miscible with Water.* — Aniline ( $C_6H_5NH_2$ ) is distilled with steam at 1 atm. The vapor-pressure of aniline is 46 mm. at  $100^\circ$  and 40 mm. at  $97^\circ$ . Water and aniline have limited solubilities in each other; one phase containing at  $100^\circ$  1.5 mol-percent of aniline, and the other 68 mol-percent of aniline. Find the boiling-point of the mixture, and the number of grams of aniline distilling over with each gram of water. Assume that the solubilities do not change appreciably within the small temperature interval, and that the vapor-pressure of the aniline in the 68 mol-percent solution is lowered only half as much as Raoult's law requires. *Ans.* 0.26 g.

$$1 - \frac{S}{S_0} = x$$

$$1 - x = \frac{S}{S_0}$$

$$S = S_0 (1 - x)$$

$$S_A = S_A^0 N_A$$

## VI. FREEZING-POINT OF SOLUTIONS

**48. Freezing-Point and Its Relation to Vapor-Pressure and Molal Composition.** — The freezing-point of a liquid is that temperature at which the solid solvent and the liquid coexist in equilibrium with each other. The solid which separates from the solution commonly consists of the pure solvent; and this is assumed to be the case throughout the following considerations. In any such case the freezing-point of a solvent is lowered by dissolving another substance in it.

At the freezing-point the vapor-pressure of the solvent in the solution and of the pure solid solvent must be equal (as shown in Prob. 49); and accordingly, from the vapor-pressure-temperature curves of the liquid solvent and solid solvent the freezing-points of solutions can be derived from their vapor-pressures (as in Prob. 50).

*Prob. 49. — Equality of the Vapor-Pressures at the Freezing-Point.* — Prove that at the freezing-point of a solution its vapor-pressure and that of the solid which separates from it must be equal, by showing that otherwise perpetual motion would result.

*Prob. 50. — Evaluation of Freezing-Points from Vapor-Pressure Data.* — The vapor-pressures of ice and (supercooled) water are as follows:

	0°	-1°	-2°	-3°	-4°
Water . . .	4.579	4.255	3.952	3.669	3.404 mm.
Ice . . .	4.579	4.215	3.879	3.566	3.277 mm.

- Calculate by Raoult's law the vapor-pressure at each of these temperatures of a solution consisting of 3 mols of solute and 97 mols of solvent. Plot on a diagram the vapor-pressures of this solution, of water, and of ice as ordinates against the temperatures as abscissas, using a scale large enough to enable 0.001 mm. to be estimated (by including on the plot pressures ranging only from 3.20 to 4.60 mm.).
- Determine from the plot the freezing-point of the solution.

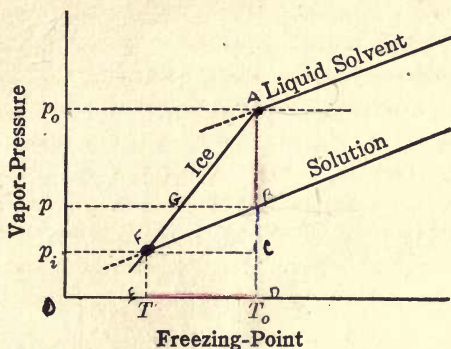
The general relations between freezing-point and vapor-pressure are illustrated by the diagram on the following page.

A consideration (as in Prob, 51) of the geometrical relations of the diagram shows that the vapor-pressure lowering  $p_0 - p$  caused by a solute is for a dilute solution related to the freezing-point lowering  $T_0 - T$  in the way expressed by the equation:

$$\frac{p_0 - p}{T_0 - T} = \frac{\partial p_s}{\partial T} - \frac{\partial p_L}{\partial T}. \quad (1)$$

In this expression the two derivatives represent the rate of change with the temperature of the vapor-pressure of the solid solvent (ice) and of the liquid solvent, respectively.

*Prob. 51. — Derivation of the Relation between Freezing-Point and Vapor-Pressure. —* From the geometrical relations of the following diagram derive equation (1) given in the text.



From the approximate Clapeyron equation (Art. 33) expressions for the temperature-coefficients of the vapor-pressures of the solid solvent and liquid solvent can be obtained in terms of the molal heats of vaporization  $\Delta\tilde{H}_S$  and  $\Delta\tilde{H}_L$  of the solid solvent and the liquid solvent, respectively. Since the difference between these two heats of vaporization can be shown by the law of initial and final states (Art. 23) to be equal to the molal heat of fusion  $\Delta\tilde{H}_0$  of the solid solvent, the following expressions, identical in form with those for the boiling-point raising (Art. 37), are readily obtained (as in Prob. 52) for the freezing-point lowering of a perfect solution:

$$T_0 - T = \frac{RT_0^2}{\Delta\tilde{H}_0} \cdot \frac{p_0 - p}{p_0} = \frac{RT_0^2}{\Delta\tilde{H}_0} \cdot \frac{\Delta t}{T_0} \quad (2)$$

In these equations  $T_0$  is the freezing-point of the solvent,  $T$  that of a solution containing the solute at the mol-fraction  $x$ , and  $\Delta\tilde{H}_0$  is the heat absorbed by the fusion of one mol of the solvent at  $T_0$ .

*Prob. 52. — Derivation of the Freezing-Point Equations for Perfect Solutions. —* Derive equation (2) from equation (1), indicating the principle involved in each step of the process, and proving that the heat of fusion is equal to the difference in the two heats of vaporization.

The quantity  $RT_0^2/\Delta\tilde{H}_0$  occurring in equation (2) is evidently a constant characteristic of the solvent. Representing this quantity, which may be called the *freezing-point constant*, by a single letter  $F_0$ , and replacing the mol-fraction  $x$  by the mol-ratio  $N/N_0$ , which becomes

identical with it as its value approaches zero, the law of freezing-point lowering for perfect solutions may be expressed by the equation:

$$T_0 - T = F_0 \frac{N}{N_0} \quad (3)$$

Instead of this freezing-point constant, the related *molal freezing-point lowering*, defined in analogy with the molal boiling-point raising (Art. 37) to be the freezing-point lowering per mol of solute in 1000 grams of solvent, is commonly recorded in chemical literature.

*Prob. 53. — Evaluation of the Freezing-Point Constants.* — When one gram of ice at 0° melts, the heat absorbed is 79.7 cal. *a.* What is the freezing-point constant for water? *b.* What is its molal freezing-point lowering? *Ans. b, 1.858 (1.86).*

\*The preceding equations are rigorously exact only when the lowerings of the freezing-point and of the vapor-pressure of the solvent are infinitesimal; for in the derivation of equation (1) all the vapor-pressure curves were regarded as straight lines, and those for the solvent and solution were regarded as parallel. A consideration of the figure at the beginning of this article shows, however, that the following differential equation, corresponding to equation (1) above, is exact for any solution whatever containing the solute at any mol-fraction  $x$  whatever:

$$\left(\frac{\partial p}{\partial x}\right)_T = \left(\frac{\partial T}{\partial x}\right)_p \left[ \left(\frac{\partial p_s}{\partial T}\right) - \left(\frac{\partial p_L}{\partial T}\right)_x \right] \quad (4)$$

\*By substituting for the first of these derivatives the expression given by the corrected Raoult equation (Art. 36), and for the last two derivatives the expressions given by the exact Clapeyron equation (Art. 33), neglecting only the volume of the solid or liquid in comparison with that of the vapor, there is obtained the following equation:

$$-dT = \frac{RT^2}{\Delta \tilde{H}} \frac{dx}{1-x} \quad (5)$$

In this equation  $-dT$  denotes the lowering produced in the freezing-point  $T$  of a solution by increasing the mol-fraction  $x$  of the solute by  $dx$ , and  $\Delta \tilde{H}$  denotes the heat absorbed by the fusion of one mol of the solid solvent into an infinite volume of the solution at its freezing-point  $T$ .

\**Prob. 54. — Freezing-Point of Solutions Conforming to Raoult's Law at Any Concentration.* — Derive equation (5) from equation (4) by the method indicated in the text.

\*This equation will be seen to correspond in form to equation (5) of Art 37 for the boiling-point raising. The equation is exact (except for the error caused by neglecting the volume of the solid or liquid in the Clapeyron equation) at any concentration up to which the corrected Raoult equation holds true. It may be integrated, usually with negligible error, under the assumption that, within the limits of temperature and concentration involved,  $\Delta\tilde{H}$  does not vary with the temperature or with the mol-fraction of the solute, and that it has the same value as the heat of fusion  $\Delta\tilde{H}_0$  of the pure solvent at its freezing-point  $T_0$ .

\*The freezing-points of solutions that do not conform to Raoult's law cannot be calculated from the molal composition. The relation between freezing-point and molal composition can, of course, be experimentally determined; and the results may be represented by freezing-point-composition diagrams, analogous to the boiling-point-composition diagrams of Art. 43. Such diagrams are considered in Chapter VIII.

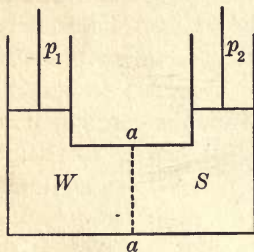
**49. Determination of Molecular Weights.** — With the aid of the laws of freezing-point lowering stated in Art. 48 the molecular weights of substances dissolved in various solvents can be calculated.

*Prob. 55. — Variation of Molecular Weight with the Nature of the Solvent.* — A solution of 0.60 g. of acetic acid in 50.0 g. of water freezes at  $-0.376^\circ$ . A solution of 2.32 g. of acetic acid in 100 g. of benzene freezes  $0.970^\circ$  lower than pure benzene. The freezing-point constant for benzene is 65.4. Calculate the molecular weight of acetic acid in each of these solvents, and state what the results show in regard to its molecular formula in each solvent.

Determinations of the molecular weights of dissolved substances by the freezing-point method have confirmed the conclusions derived from boiling-point determinations, and stated in Art. 38, as to the dissociating effect of various solvents.

## VII. OSMOTIC PRESSURE OF SOLUTIONS

**50. Osmotic Pressure.** — When a solution  $S$  is separated from a pure solvent  $W$ , as illustrated in the figure, by a wall  $aa$  which allows this solvent to pass through it, but prevents entirely the passage of the solute, the solvent is drawn through the wall into the solution. This flow of solvent may, however, be prevented by exerting a pressure  $p_2$  on the solution greater by a definite amount than the pressure  $p_1$  upon the pure solvent; and the solvent may be forced out of the solution by exerting a still greater pressure upon the



solution. The difference of pressures on solution and solvent which produces a condition of equilibrium such that there is no tendency of the solvent to flow in either direction is called the *osmotic pressure*  $P$  of the solution.

Walls of the kind just described are known as *semipermeable walls*. Certain animal membranes, such as parchment or bladder, are permeable for water, but not for certain solutes of high molecular weight (the so-called colloids). The walls of some animal and plant cells are very perfect semipermeable walls. The most satisfactory artificial semipermeable walls have been made by precipitating copper ferrocyanide within the pores of an unglazed porcelain cell, which gives the precipitate sufficient rigidity to withstand high osmotic pressures. The cell, filled with the solution and immersed in pure water, is connected with a manometer whose mercury column is in direct contact with the solution. By means of such cells exact measurements of the osmotic pressure of aqueous solutions of cane-sugar and glucose have been made up to pressures of 230 atmospheres.

Osmotic pressure plays a very important part in the physiological processes taking place in the bodies of animals and plants. In the study of the general principles of chemistry, it is of value because it is a property which, like vapor-pressure, enables the various properties of solutions to be correlated and their energy relations to be treated upon the basis of one simple fundamental concept. The correspondence shown in Art. 52 to exist between the laws of the osmotic pressure of dilute solutions and those of the pressure of perfect gases makes possible, moreover, a closely analogous treatment of these two states.

**\*51. Relation of Osmotic Pressure to Vapor-Pressure.** — In the osmotic arrangement represented in the figure of Art. 50, when the pressures  $p_1$  and  $p_2$  are such that there is equilibrium and therefore no tendency for the solvent to pass through the semipermeable wall, it follows from the perpetual motion principle that the vapor-pressure of the solvent in the pure state must be equal to its vapor-pressure in the solution. For, if a vapor phase were in contact (through walls permeable only for the vapor) both with the solvent and the solution, there would evidently be a continuous flow of the solvent-substance through the vapor-phase and back through the wall between the two liquid phases, unless its vapor-pressures in these liquid phases were equal. That this condition is realized results from the fact that the vapor-pressure of a liquid is increased by increasing the pressure upon it. Thus the larger pressure  $p_2$  on the solution increases its vapor-pressure up to the value of the vapor-pressure of the solvent under the smaller pressure  $p_1$ .

The effect of pressure on vapor-pressure may be now considered from a quantitative standpoint. It can be shown (as in Prob. 56) that the increase  $dp$  in the vapor-pressure  $p$  of a liquid caused by an increase  $dp_L$  in the pressure  $p_L$  on the liquid is expressed by the following equation, in which  $v_L$  represents the volume of any definite weight of the liquid at the pressure  $p_L$ , and  $v$  represents the volume of the same weight of the vapor at the pressure  $p$ :

$$dp = \frac{v_L}{v} dp_L. \quad (1)$$

In case the vapor may be regarded as a perfect gas, this equation takes the following form, in which  $\tilde{v}_L$  represents the volume of one mol of the liquid at the pressure  $p_L$ :

$$\frac{dp}{p} = \frac{\tilde{v}_L}{RT} dp_L. \quad (2)$$

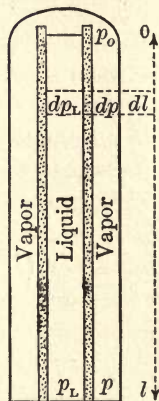
By integration of this equation under the assumption that the volume of the liquid,  $\tilde{v}_L$ , does not change with the pressure there results the following expression, in which  $p$  and  $p_0$  denote the vapor-pressures of the solvent when the pressures on it are  $p_L$  and zero, respectively:

$$\log \frac{p}{p_0} = \frac{p_L \tilde{v}_L}{RT}. \quad (3)$$

*Effect of Pressure on the Vapor-Pressure of Liquids. —*

*Prob. 56.* — Consider, as illustrated in the figure, a column of a pure liquid contained in a porous tube impermeable to it, but permeable to its vapor; and consider this tube to be surrounded by the vapor of the liquid; the whole system being at a constant temperature  $T$ . When there is equilibrium the vapor-pressure of the liquid at any level must evidently be equal to the pressure of the vapor at that level. The pressure of the liquid or of the vapor must, however, be greater at a lower than a higher level by the (hydrostatic) pressure of the intervening column of liquid or vapor.

*a.* Formulate an expression for the increase  $dp_L$  of the pressure  $p_L$  of the liquid, and one for the increase  $dp$  of the pressure  $p$  of the vapor, corresponding to an increase  $dl$  in the distance  $l$  beneath the surface. *b.* By combining these expressions, derive equation (1) given in the text. *c.* Integrate this equation, assuming that the vapor conforms to the perfect-gas laws and that the volume of the liquid does not vary with the pressure upon it, so as to obtain a relation between the vapor-pressures  $p_0$  and  $p$  of the liquid at the top and bottom of the column in terms of its hydrostatic pressure  $p_L$ .



*Prob. 57.* — Find the ratio of the vapor-pressure of water at  $4^\circ$  and 10 atm. to that at  $4^\circ$  and the pressure (6 mm.) of the saturated vapor.

It is evident now that, by applying a sufficient negative pressure (or suction) to a liquid solvent, its vapor-pressure can be reduced from its normal value  $p_0$  to the value  $p$  which it normally has in any definite solution, and that then it would be in equilibrium with that solution if placed in communication with it through a semipermeable wall. (Liquids can in fact with suitable precautions be subjected to negative pressures of many atmospheres, without the column breaking.) The difference in the pressures on the solution and the solvent, defined to be the osmotic pressure  $P$ , is evidently numerically equal to this pressure  $p_L$  applied to the solvent, but opposite in sign; that is,  $P = -p_L$ . Hence it follows from equation (3) that the osmotic pressure at the temperature  $T$  of a solution in a solvent whose vapor-pressure is  $p$  in the solution and  $p_0$  in the pure state, and whose molal volume is  $\tilde{v}_L$ , is given by the expression:

$$P = \frac{RT}{\tilde{v}_L} \log \frac{p_0}{p}. \quad (4)$$

This expression is exact even at large concentrations provided the vapor conforms to the perfect-gas laws, except for the usually negligible effect of pressure on the volume  $\tilde{v}_L$  of the solvent.

*Relation of Osmotic Pressure to Vapor-Pressure. —*

*Prob. 58. — a.* How much must the pressure on water be reduced in order that it may be in equilibrium through a semipermeable wall with an aqueous solution which has at  $25^{\circ}$  a vapor-pressure 98% as great as that of water? *b.* What is the osmotic pressure of this solution at  $25^{\circ}$ ?

*Prob. 59. —* At  $100^{\circ}$  the vapor-pressure of a solution consisting of 28 g. of NaCl and 100 g. of water is 624 mm. What is its osmotic pressure? The specific volume of water at  $100^{\circ}$  is 1.043. *Ans.* 320 atm.

When the vapor does not conform to the perfect-gas laws an exact expression may be readily obtained by substituting for  $v$  in equation (1) the expression  $RT(1 + \alpha p)/p$  given by the equation of state for gases at moderate pressure (Art. 15), and integrating as before. This leads to the result that the osmotic pressure equation may be corrected for deviation of the vapor from the perfect-gas laws by writing it in the form:

$$P = \frac{RT}{\tilde{v}_L} \left( \log \frac{p_0}{p} + \alpha(p_0 - p) \right). \quad (5)$$

**52. Relation between Osmotic Pressure and Molal Composition. —**

The osmotic pressure  $P$  of concentrated solutions whose vapor-pressure conforms to Raoult's law is expressed by the following equation, which may readily be derived (as shown in Prob. 60) from equation (4) or (5) of Art. 51.

$$P\tilde{v}_L = RT \log \left( 1 + \frac{N}{N_0} \right). \quad (1)$$

In this equation  $\tilde{v}_L$  represents the molal volume of the solvent, and  $N$  denotes the number of mols of solute associated with  $N_0$  mols of solvent.

For dilute solutions, for which  $N/N_0$  is small, this equation can be simplified (as shown in Prob. 61) by expanding the logarithm into a series, neglecting all the terms except the first one, and transforming. The following expression then results:

$$P v_0 = NRT. \quad (2)$$

In this expression  $P$  is the osmotic pressure at the temperature  $T$  of a solution consisting of  $N$  mols of solute and  $N_0$  mols of solvent whose volume in the pure state is  $v_0$ , and  $R$  is the gas-constant.

This equation is seen not only to be identical in form with the perfect-gas equation, but to contain the same constant  $R$ . This shows that a substance in dilute solution produces an osmotic pressure which is equal to the pressure it exerts at the same temperature as a perfect gas when present at the same volume concentration.

The osmotic pressure of concentrated solutions to which Raoult's law does not apply cannot be calculated from the composition of the solution. It may, however, be determined not only by direct measurement, but also by calculation from vapor-pressure measurements, by equations (4) and (5) of Art. 51.

*Derivation of the Osmotic-Pressure Equations. —*

\**Prob. 60.* — Derive equation (1) of this article,  $a$ , from equation (4), and  $b$ , from equation (5) of Art. 51.

*Prob. 61.* — Derive equation (2) from equation (1) in the way indicated in the above text.

*Prob. 62. — Osmotic Pressure in Relation to Hydrostatic Pressure. —* The lower end of a vertical tube is closed with a semipermeable wall and is dipped just beneath the surface of pure water. A 0.1 molal solution of cane-sugar ( $C_{12}H_{22}O_{11}$ ) of density 1.014 is poured into the tube until the hydrostatic pressure at the semipermeable wall is sufficient to prevent water from entering the solution. The temperature is  $4^{\circ}$ . Find the height of the column in meters. *Ans.* 23.6

# VIII. REVIEW OF THE PRINCIPLES RELATING TO THE MOLAL PROPERTIES OF SOLUTIONS

**53. Review Problems.** — The following problems afford a review and give additional applications of the principles relating to the molal properties of solutions.

*Prob. 63. — a.* Summarize the equations expressing for dilute solutions the approximate relations between molal composition and (1) vapor-pressure, (2) boiling-point, (3) freezing-point, (4) osmotic pressure. State explicitly what each symbol signifies.

*\*Prob. 64. —* Summarize the corresponding equations which hold true for perfect solutions of any concentration.

*Prob. 65. —* Calculate by the laws of dilute solutions the fractional vapor-pressure lowering, the boiling-point raising, the freezing-point lowering, and the osmotic pressure at  $5.5^{\circ}$ , of a solution containing 0.1 mol of a nonvolatile solute in 1000 g. of benzene, with the aid of the following data. The heat of fusion of one gram of benzene at its freezing-point,  $5.5^{\circ}$ , is 30.2 cal. The heat of vaporization of one gram of benzene at its boiling-point,  $80.1^{\circ}$ , is 93.0 cal. The density at the freezing-point is 0.895.

*\*Prob. 66. — a.* Calculate by the laws of concentrated perfect solutions the fractional vapor-pressure lowering, the boiling-point raising, the freezing-point lowering, and the osmotic pressure at  $5.5^{\circ}$ , of a solution containing 2 mols of a non-volatile solute in 1000 g. of benzene, using the data of Prob. 65, and assuming that the vapor conforms to the perfect-gas laws. *b.* Calculate the ratio of each of these values to the corresponding one for the solution of Prob. 65. (Note that the value of this ratio would be 20.0 if the equations for dilute solutions were applicable to this concentrated solution.) *c.* Assuming the solute to be volatile and to have a partial vapor-pressure of 20 mm. in the solution at its boiling-point, calculate this boiling-point. *Ans. c,*  $84.2^{\circ}$ .

*Prob. 67. — a.* Carbon bisulfide boils at  $46^{\circ}$  at 1 atm. Its molal heat of vaporization at this temperature is 6430 cal. What is its boiling-point constant? *b.* A solution of 15.5 g. of phosphorus (at. wt., 31.0) in 1000 g. of  $\text{CS}_2$  boils  $0.300^{\circ}$  higher than pure  $\text{CS}_2$ . What is the molecular weight and what is the molecular formula of phosphorus in this solvent?

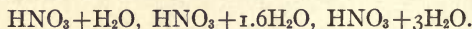
*\*Prob. 68. —* If 127 g. of iodine (at. wt., 127) were added to the solution of Prob. 67*b*, how much higher than the boiling-point of pure  $\text{CS}_2$  would that of the solution be: *a*, in case the iodine remained uncombined in the form of  $\text{I}_2$ ; *b*, in case it all combined with the phosphorus forming  $\text{P}_4\text{I}_8$ ; *c*, forming  $\text{P}_2\text{I}_4$ ; *d*, forming  $\text{PI}_3$ ?

*\*Prob. 69. —* Human blood freezes at  $-0.56^{\circ}$ . Find its osmotic pressure at  $37^{\circ}$ . *Ans.* 7.6 atm.

*\*Prob. 70. —* At  $25^{\circ}$  the distribution-ratio of  $\text{Br}_2$  between carbon tetrachloride and water is 38 expressed in volume concentrations; and the pressure of bromine above a 0.05 molal solution of  $\text{Br}_2$  in water is

50 mm. Assuming that one liter of this solution is shaken with 50 ccm. of carbon tetrachloride, calculate the pressure of the bromine over the carbon-tetrachloride phase. (Bromine exists in all three phases only as  $\text{Br}_2$ .) *Ans.* 17.2 mm.

*Prob. 71.* — At 1 atm. pure nitric acid has a boiling-point of  $86^\circ$ . A solution of nitric acid and water of the composition  $\text{HNO}_3 + 1.6\text{H}_2\text{O}$  distills at 1 atm. at a constant temperature of  $121^\circ$ . Make a diagram showing the character of the boiling-point-composition curve for this pair of substances. Draw in on the diagram a curve representing in a general way the composition of the vapor in equilibrium with any solution at its boiling-point. State what products would finally result as distillate and residue from the fractionation of the three solutions,



*Prob. 72.* — Upon partial distillation at constant pressure a solution of two components A and B containing 20% of A, having a boiling-point of  $80^\circ$ , yields a residue containing 15% of A; and a mixture containing 75% of A, having a boiling-point of  $60^\circ$ , yields a distillate containing 70% of A. Draw a diagram which will show in a general way the character of the liquid-composition and of the vapor-composition curve. Predict what products would finally result as distillate and residue from the fractionation of the 20% and of the 75% solution.

## CHAPTER IV

### THE ATOMIC PROPERTIES OF SOLID SUBSTANCES

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#### I. THE HEAT-CAPACITY OF SOLID SUBSTANCES

**54. Properties in the Solid State.** — Many of the properties of substances in the gaseous and dissolved states are primarily determined, as has been shown in the preceding chapters, by the number of molecules present; but in the solid state such molal properties are met with only in the case of substances present at small concentration in solid solutions (considered in Art. 123). In the solid state there are, however, certain properties, here called *atomic properties*, which depend primarily either on the number of atoms present in the unit-weight of the substance, or on the number of atoms present in each molecule of the substance. The heat-capacity of solid substances is a property of the first of these types; and *isomorphism*, or the power of two substances of assuming nearly the same crystal structure and of forming with each other a continuous series of solid solutions, is a property of the second of these types. The heat-capacity of solid substances, which is of importance not only in its relations to the atomic theory, but also in thermodynamic considerations, will alone be considered here.

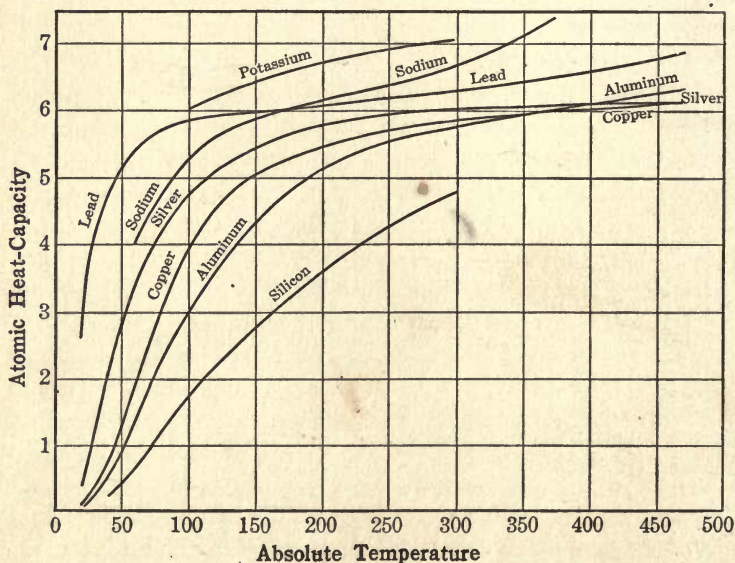
**55. The Heat-Capacity of Solid Elementary Substances.** — Measurements have shown that at room temperature all elementary substances with atomic weights above 35, and the metallic elementary substances with smaller atomic weights than 35, have values of the atomic heat-capacity (defined as in Art. 25) not differing greatly from each other. This approximate principle is known as *Dulong and Petit's law*.

The average value of the atomic heat-capacity at constant pressure at 20° for these elements is 6.2 calories per degree. Deviations of  $\pm 0.4$  unit are not uncommon; and deviations of  $+0.5$  to  $+0.9$  unit are exhibited by some elements (for example, by sodium, potassium and iodine) which at room temperature are not much below their melting-points. In the case of the non-metallic elements with smaller atomic weights than 35 the atomic heat-capacity has a value much smaller than 6.2 at room temperature; thus the value for boron is 2.6, for graphite 1.9, for silicon 4.8, for phosphorus 5.6, and for sulphur 5.5.

The corresponding average value of the atomic heat-capacity at constant volume at room temperature is 5.9; and from this simpler, more fundamental quantity the values for the separate substances show considerably smaller deviations.

It is interesting to note that this average atomic heat-capacity is very nearly twice the translatory kinetic energy (2.98 cal.) taken up per degree by the molecules of a gaseous or liquid substance (Art. 19). The kinetic factors determining this roughly constant value for solid elementary substances, and causing the marked variation of the heat-capacity with the temperature to be now mentioned, are too complex and hypothetical to be here considered.

The effect of temperature on the atomic heat-capacity at constant pressure is shown in the figure. It will be seen that at very low temperatures (below 200° A) the atomic heat-capacity of solid elementary substances varies much with the nature of the substance and is always much smaller than at room temperature; that with rising temperature it increases at different rates in the case of different substances; and that at a temperature, varying with the different substances but usually not far from the room temperature, it attains the average value, and then as a rule increases only slowly with further increase of temperature.



**56. The Heat-Capacity of Solid Compound Substances.** — Another roughly approximate principle, called *Kopp's law*, has been found experimentally to express the heat-capacity of solid inorganic compounds at room temperature. It has been found, namely, that the formal heat-capacity is approximately an *additive property*, that is, one whose value can be approximately calculated by adding together certain values representing the heat-capacity of the elements contained in the compound. This principle is expressed by the following equation, which shows at the same time the values of the constants (the so-called atomic heat-capacities) for the common elements:

$$\tilde{C}_p = 6.2 n_E + 4.0 n_O + 2.3 n_H + 1.8 n_C + 5.4 n_S + 2.3 n_B + 5.4 n_P + 3.8 n_{Si}.$$

In this equation  $\tilde{C}_p$  represents the formal heat-capacity of the compound at constant pressure at room temperature;  $n_O$ ,  $n_H$ ,  $n_C$ ,  $n_S$ ,  $n_B$ ,  $n_P$ , and  $n_{Si}$  are the number of atomic weights of oxygen, hydrogen, carbon, sulfur, boron, phosphorus, and silicon present in one formula-weight of the compound; and  $n_E$  is the number of atomic weights of any other element so present. The values given for the constants are average values derived from heat-capacity measurements with solid compounds. They do not accurately represent the atomic heat-capacities of the solid elementary substances.

The following table illustrates the degree of correspondence which exists between the values of the formal heat-capacity so calculated and those measured experimentally. It will be observed that differences of ten percent between the calculated and measured values are not uncommon.

HEAT-CAPACITIES OF SOLID COMPOUND SUBSTANCES

Substance	Calc.	Meas.	Substance	Calc.	Meas.
H <sub>2</sub> O (ice)	8.6	9.1	PbN <sub>2</sub> O <sub>6</sub>	42.6	38.8
Al <sub>2</sub> O <sub>3</sub>	24.4	20.5	CaSiO <sub>3</sub>	22.0	21.3
Fe <sub>2</sub> O <sub>3</sub>	24.4	25.6	K <sub>4</sub> Fe(CN) <sub>6</sub>	79.0	79.0
Sb <sub>2</sub> S <sub>3</sub>	28.6	28.7	CuSO <sub>4</sub>	27.6	25.8
KCl	12.4	12.4	CuSO <sub>4</sub> ·5H <sub>2</sub> O	70.6	72.7
PbCl <sub>2</sub>	18.6	18.2	AlK(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	158.	165.
CaCO <sub>3</sub>	20.0	20.2	NH <sub>4</sub> Cl	21.6	19.9
KClO <sub>3</sub>	24.4	24.1	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	24.2	25.1

*Prob. 1. — Specific Heat-Capacities Calculated by the Additivity Principle.* — Calculate an approximate value at 20° of the specific heat-capacity at constant pressure of: *a*, platinum; *b*, silver bromide; *c*, potassium sulfate. Find the percentage deviations of these values from the measured values, which are, *a*, 0.032; *b*, 0.074; *c*, 0.190.

**57. Determination of Atomic Weights.** — The law of Dulong and Petit, even though it is only an approximate principle, may evidently be employed for determining what multiple of the combining weight of an element is its atomic weight; and the application of this law was in fact one of the most important methods by which the present system of atomic weight values was established.

*Prob. 2. — Determination of Atomic Weights.* — Calculate the exact atomic weight of an element whose specific heat-capacity is 0.092 and whose oxide contains 88.82% of the element.

## II. GENERALIZATIONS RELATING TO ATOMIC WEIGHTS

**58. The Methods of Atomic Weight Determination and the Periodic Law.** — The important methods already considered for determining what multiple of the combining weight is the atomic weight may now be briefly summarized.

It was shown in Art. 14 that the atomic weight of an element, or at any rate a maximum value for its atomic weight, can be obtained by finding the smallest weight of the element contained in one molecular weight of any of its gaseous compounds, as derived from the density and Avogadro's principle. Molecular weights derived from the laws of perfect solutions (Arts. 36, 38, 49) may also be used for the same purpose.

It was shown in Art. 27 that the molal heat-capacity of perfect gases is dependent on the number of atoms in the molecule, that this property has a definite value predicted by the kinetic theory for gases with monatomic molecules, and that therefore the atomic weight of elements which form gases having this molal heat-capacity can be immediately derived from their gas densities and the corresponding molecular weights.

It was shown in Art. 57 that the atomic weight of elements can be directly determined from the principle that the atomic heat-capacities of solid elementary substances at room temperature have approximately the same value. Finally, atomic weights can also be derived from the phenomenon of isomorphism mentioned in Art. 54.

By a combination of all these methods, which have in general given concordant results, the present system of atomic weight values has been derived.

When the elements are arranged in the order of the so determined atomic weights, it is found that there is a progressive change in the various properties of the elementary substances and their compounds, and a periodic recurrence of similar properties. This generalization is called the *periodic law*; and many systematic arrangements of the elements have been proposed for the purpose of bringing out as fully as possible the relations between their properties. These relations are most appropriately considered in the detailed study of inorganic chemistry, and are therefore only briefly referred to here.

## CHAPTER V

### THE ELECTROLYTIC BEHAVIOR OF SOLUTIONS AND THE IONIC THEORY

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#### I. THE MOLAL PROPERTIES OF SOLUTIONS OF IONIZED SUBSTANCES

**59. Effects of Salts on the Molal Properties of Aqueous Solutions and Their Explanation by the Ionic Theory.** — In dilute solution the effect of salts of the uniunivalent type, such as sodium chloride or silver nitrate, on the vapor-pressure of water and on the other related molal properties is nearly twice as great, and the effect of salts of the unibivalent type, such as potassium sulfate and barium chloride, is nearly three times as great, as it would be if each formula-weight yielded a single mol in the solution. Strong acids and bases show a similar behavior.

The following values illustrate the effect of some typical ionized substances on the freezing-point of water at a concentration 0.1 formal. The value given is the ratio, called the *mol-number* (*i*), of the effect produced by one formula-weight of the substance to that produced by one mol of a perfect solute.

NaCl, 1.87; NaNO<sub>3</sub>, 1.83; KClO<sub>3</sub>, 1.80; HCl, 1.92; MgSO<sub>4</sub>, 1.32;

BaCl<sub>2</sub>, 2.58; Pb(NO<sub>3</sub>)<sub>2</sub>, 2.30; Na<sub>2</sub>SO<sub>4</sub>, 2.47; K<sub>4</sub>Fe(CN)<sub>6</sub>, 3.32.

As the concentration decreases the value of the mol-number approaches 2 for the uniunivalent substances, and 3 for the unibivalent substances.

These and other facts have led to the conclusion that these substances are largely dissociated in aqueous solution. For example, NaCl dissociates into Na<sup>+</sup> and Cl<sup>-</sup>; HNO<sub>3</sub> into H<sup>+</sup> and NO<sub>3</sub><sup>-</sup>; H<sub>2</sub>SO<sub>4</sub> into H<sup>+</sup>, H<sup>+</sup>, and SO<sub>4</sub><sup>=</sup>; and Ba(OH)<sub>2</sub> into Ba<sup>++</sup>, OH<sup>-</sup>, and OH<sup>-</sup>. Tri-ionic substances may also dissociate partially into intermediate ions; thus H<sub>2</sub>SO<sub>4</sub> into HSO<sub>4</sub><sup>-</sup> (and H<sup>+</sup>).

The electrical behavior of the solutions indicates that these dissociation-products differ from ordinary substances in that their molecules are electrically charged. These charged molecules are called *ions*; and to their formulas + or - signs are attached, as in the above examples, to indicate the nature and magnitude of the charge. The fraction of the salt dissociated is called its *ionization*  $\gamma$ . This fraction always decreases with increasing concentration.

From the effect of ionized substances on the molal properties their ionization has often been calculated. The evidence, however, seems to show that ions produce on the vapor-pressure, boiling-point, and freezing-point of water, even at moderate concentrations such as 0.1 molal, effects which differ considerably from those produced by perfect solutes at the same molal concentration. These deviations, which will be more fully considered in Art. 79, make unreliable the exact computation of the ionization of salts from the vapor-pressure and freezing-point lowering. In spite of the deviations a rough estimate of the number of mols of solute present in solutions of ionized substances can be derived from the results of measurements of the molal properties, with the aid of the laws of perfect solutions; and such measurements often furnish useful information as to the forms in which substances exist in the solution.

*Prob. 1. — Effect of Salts on the Molal Properties.* — A solution of 0.65 formula-weight of KCl in 1000 g. of water has at  $100^{\circ}$  a vapor-pressure of 744.8 mm. *a.* Calculate the mol-number  $i$ , which expresses the ratio of the observed lowering to that which would be produced by 0.65 mol of a perfect solute in 1000 g. of water. *b.* Find the ionization of the salt to which this value of  $i$  would correspond if the ions acted as perfect solutes.

*Prob. 2. — Determination of the Chemical Substances Present in Solutions.* — The freezing-point of a solution containing 0.05 formula-weights of  $\text{H}_2\text{SO}_4$  per 1000 g. of water is  $-0.215^{\circ}$ . *a.* Find the corresponding value of the mol-number  $i$ . *b.* Derive from this value an estimate of the secondary ionization of the  $\text{HSO}_4^-$  into  $\text{H}^+$  and  $\text{SO}_4^{=}$ , assuming that the primary ionization of the  $\text{H}_2\text{SO}_4$  into  $\text{H}^+$  and  $\text{HSO}_4^-$  is complete and that the ions act as perfect solutes.

## II. ELECTROLYSIS AND FARADAY'S LAW

**60. Electrolytic Conduction.** — Conductors are divided into two classes with reference to the changes that are produced in them by the passage of electric currents. Those which undergo no changes except such as are produced by a rise in temperature are called *metallic conductors*. Those in which the passage of a current is attended by a chemical change are called *electrolytes*. Aqueous solutions of salts, bases, and acids, and melted salts at high temperatures, are the most important classes of the well-conducting electrolytes. The most obvious chemical changes attending the passage of a current through an electrolyte are those that take place at the surfaces of the metallic conductors where the current enters and leaves the electrolyte. The production of such chemical changes by a current from an external source is called *electrolysis*. The occurrence of such changes, when they themselves give rise to an electric current, is called *voltaic action*. Those portions of the metallic conductors that are in contact with the electrolyte are called the *electrodes*; the one at which the current leaves the electrolyte, or the one towards which the positive electricity flows through the electrolyte, is designated the *cathode*; the other, the *anode*.

**61. Chemical Changes at the Electrodes.** — The chemical change produced at the cathode is always a reduction; that at the anode, an oxidation. The following table exemplifies types of chemical changes commonly occurring in electrolysis. It shows the products resulting when aqueous solutions of certain typical salts, bases, and acids are electrolyzed between electrodes which are unattacked, for example, between platinum or carbon electrodes.

THE PRODUCTS OF ELECTROLYSIS

<i>Solute</i>	<i>Cathode products</i>	<i>Anode products</i>
$\text{Cu}(\text{NO}_3)_2$ or $\text{AgNO}_3$	Cu or Ag	$\text{O}_2$ and $\text{HNO}_3$
$\text{KNO}_3$	$\text{H}_2$ and KOH	$\text{O}_2$ and $\text{HNO}_3$
$\text{Na}_2\text{SO}_4$	$\text{H}_2$ and NaOH	$\text{O}_2$ and $\text{H}_2\text{SO}_4$
KOH or $\text{Ba}(\text{OH})_2$	$\text{H}_2$	$\text{O}_2$
$\text{H}_2\text{SO}_4$ or $\text{H}_3\text{PO}_4$	$\text{H}_2$	$\text{O}_2$
Dilute HCl or $\text{HNO}_3$	$\text{H}_2$	$\text{O}_2$
Concentrated HCl	$\text{H}_2$	$\text{Cl}_2$

When the anode is a metal which can react with the anion of the solute, the change at the anode may consist only in the dissolving of the metal; thus when a nitrate or sulfate is electrolyzed with a

copper anode, copper passes into solution, forming copper nitrate or sulfate.

When the cathode is coated with a reducible solid substance, such as silver chloride or lead dioxide, or is surrounded with a solution containing a reducible solute, such as a ferric salt or a chromate, this substance is reduced and there may be no hydrogen evolved. In any definite electrolytic cell, however, the nature of the changes at the electrodes often varies with the conditions of the electrolysis, such as the applied electromotive force, current-density, concentration, and temperature.

In the case of voltaic actions, the chemical changes are of a similar character, most commonly consisting in the solution of the metal composing the anode, and in the deposition of another metal or of hydrogen on the cathode or in the production of a soluble reduced substance at the cathode. Thus, in the Daniell cell, which consists of a copper electrode in a copper sulfate solution and of a zinc electrode in a zinc sulfate solution, the two solutions being in contact and the two electrodes connected by a metallic conductor, the zinc dissolves and the copper precipitates; and, in the Bunsen cell, consisting of a zinc electrode in dilute sulfuric acid and a carbon electrode in strong nitric acid, zinc dissolves at the anode, and the hydrogen primarily produced at the cathode reduces the nitric acid to lower oxides of nitrogen.

*Prob. 3. — Changes at the Electrodes. —* State what substances are produced or destroyed at each electrode when electricity passes through: *a*, a concentrated solution of NaCl between a carbon anode and an iron cathode; *b*, a solution of NaCl between a silver anode and a metal cathode coated with AgCl; *c*, dilute  $\text{H}_2\text{SO}_4$  between a lead anode and a cathode of lead coated with  $\text{PbO}_2$ ; *d*, a solution of  $\text{ZnSO}_4$  between a zinc-amalgam anode and a cathode of mercury covered with  $\text{Hg}_2\text{SO}_4$ ; *e*, through a solution of  $\text{K}_2\text{SO}_4$  between platinum electrodes.

**62. Faraday's Law.** — The passage of electricity through an electrolyte is attended at each electrode by a chemical change involving a number of chemical equivalents  $N$  strictly proportional to the quantity of electricity  $Q$  passed through and dependent on that alone. That is:  $Q = FN$ , where  $F$  is a constant with respect to all variations of the conditions, such as temperature, concentration, current-strength, current-density, etc. Such variations often influence the character of the chemical change, but not the total number of equivalents

involved. The law is applicable to concentrated, as well as to dilute solutions, and to fused salts. It is known as *Faraday's law*.

The constant  $F$  evidently represents the quantity of electricity producing a chemical change involving one equivalent. It is called a *faraday*, and has the value 96,500 coulombs. One *coulomb* is the quantity of electricity flowing per second when the current is one *ampere*.

The term chemical equivalent in the above statement of Faraday's law signifies the oxidation or reduction equivalent of the substance in the sense in which it is used in volumetric analysis. That is, *one equivalent* of any substance is that weight of it which is capable of oxidizing one atomic weight of hydrogen, or which has the same reducing power as one atomic weight of hydrogen.

*Applications of Faraday's Law.* —

✓ *Prob. 4.* — Through solutions of  $\text{AgNO}_3$ ,  $\text{BiCl}_3$ ,  $\text{Hg}_2\text{SO}_4$ , and  $\text{PbCl}_2$ , placed in series, 9650 coulombs are passed. How many grams of metal will be deposited on the cathode from each solution?

*Prob. 5.* — A Daniell cell, consisting of zinc in  $\text{ZnSO}_4$  solution and copper in  $\text{CuSO}_4$  solution, furnishes a current of 0.1 ampere for 100 minutes. How many grams of copper deposit and of zinc dissolve in the cell?

✓ *Prob. 6.* — How long must a current of 5 amperes be passed through dilute sulphuric acid in order to produce at  $27^\circ$  and 1 atm., *a*, one liter of oxygen? *b*, one liter of hydrogen? *Ans. a*, 52.3 min.

*Prob. 7.* — 1930 coulombs are passed through a solution of  $\text{CuSO}_4$ . At the cathode 0.018 equivalent of copper is deposited. How many equivalents of hydrogen are set free?

**63. The Mechanism of Conduction between Electrodes and Solutions.** — Faraday's law evidently shows that electricity is transferred from solution to electrode, or in the reverse direction, only by the constituents of the electrolyte; and that one equivalent of any constituent carries the same quantity of electricity, namely, one faraday or 96500 coulombs. These current-carrying constituents, called the *ion-constituents*, exist, according to the ionic theory, partly combined with one another as substances whose molecules are electrically neutral, and partly as separate substances whose molecules are electrically charged. These charged molecules, and also the substances consisting of them, are called *ions*, — the positively charged ones *cations*, and the negatively charged ones *anions*. When it is necessary to distinguish between the charged substance and the charged molecule, the terms ion-substance and ion-molecule will be used.

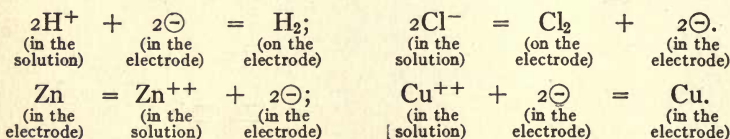
Faraday's law gives no indication as to which of the ions that may be present in the solution are involved in the chemical changes at the electrodes. It is not in general true either that only one kind of ion or that all the kinds of ions present are discharged or produced at the electrodes. Even those ions which are most concentrated in the solution may not be involved at all in the chemical change at the electrode. Thus in electrolyzing a concentrated sodium chloride solution, there are discharged at the cathode not the sodium ions of the salt, but the hydrogen ions of the water, even though these have only a very slight concentration in the solution. Moreover, the transfer of electricity to the cathode may be effected, not only by the deposition of a cation, but also by the formation of an anion, as in the case of an iodine electrode; for flow of negative electricity in one direction produces a current having the same electrical effects as flow of positive electricity in the other. The factors that determine which ions are involved in the electrode processes will be considered in Chapter XI.

Since one mol of any ion-substance has a charge of 96,500 coulombs or some simple multiple of this quantity of electricity, and since it consists of a definite number of molecules, the Avogadro number,  $6.06 \times 10^{23}$  (Art. 19), any ion-molecule must have a charge which is equal to or a simple multiple of a definite quantity of electricity, namely,  $96,500 / (6.06 \times 10^{23})$  or  $1.59 \times 10^{-19}$  coulomb. This is evidently a quantity of electricity, which, like an atom of an element, is not subdivided in chemical processes. This quantity of negative electricity is called a *negative electron*, or often simply an *electron*; the corresponding quantity of positive electricity is called a *positive electron*.

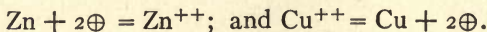
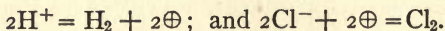
Negative electrons are capable of existing as separate particles; thus cathode rays, and the beta rays emitted by radioactive substances, have been shown to consist of a stream of such electrons. But positive electrons are known only in association with atoms or molecules. Since only the negative electron is known to detach itself from matter, anions are regarded as combinations of neutral atoms or atom-groups with one or more negative electrons, and cations as neutral atoms or atom-groups which have lost one or more negative electrons. Moreover, since there is no transfer of matter in metallic conduction, the current is carried through the metal solely by negative electrons.

In accordance with these views, the mechanism of conduction between electrodes and solutions consists in a passage of ions to or from the electrode and the taking up or giving off by the electrode of negative electrons, these being continuously removed or supplied at its surface by their flow through the metallic conductor. Thus in the electrolysis of hydrochloric acid, hydrogen ions move from the solution to the cathode and take up there negative electrons, thereby producing neutral hydrogen molecules; and chloride ions move from the solution to the anode and give off there negative electrons, thereby producing neutral chlorine molecules. Similarly in the Daniell cell, neutral zinc atoms in the anode give up to it negative electrons and pass into the solution in the form of zinc ions, and copper ions move to the cathode from the solution, and take up negative electrons from the cathode, thereby becoming neutral copper atoms.

The chemical changes and the accompanying electrical effects taking place at the electrodes in the way just described may be represented by *electrochemical equations*, in which a free negative electron in the electrode is represented by the symbol  $\ominus$ . Thus, the electrochemical equations for the processes considered above are:



Since it has long been customary to consider an electric current as a flow of positive electricity, it is usually more convenient to express the effects at the electrodes as if they involved positive electrons, which are denoted by the symbol  $\oplus$ . Thus the above electrode effects are expressed by the equations:



Furthermore, it is usually advantageous to write the equations so as to show the substances that are actually produced or destroyed, and not merely the ions that are directly concerned in the mechanism of the electrode process. Thus the cathode process in the electrolytic decomposition of water (in the presence of a sodium salt) would be expressed by the equation  $2\text{H}_2\text{O} = \text{H}_2 + 2\text{OH}^- + 2\oplus$ , and not simply by the equation  $2\text{H}^+ = \text{H}_2 + 2\oplus$ . In these electrochemical equations,

as in other chemical equations, the formulas may represent either the molecules and electrons, or the mols of the substances and the faradays of electricity.

*Prob. 8. — Formulation of Cells and Electrochemical Equations. —*

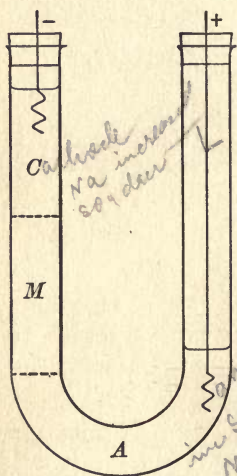
*a.* Formulate (as in the answer given below) the five cells described in Prob. 3, showing also the substances produced at the electrodes.

*b.* Write electrochemical equations expressing the chemical changes and electrical effects at each of the electrodes when one faraday passes through each of these cells. *Ans.* First cell: *a*,  $C + Cl_2, Na^+Cl^-$  (conc.)

in  $H_2O, H_2 + Fe$ . *b*,  $Cl^- + \oplus = \frac{1}{2}Cl_2$ ;  $H_2O = \frac{1}{2}H_2 + OH^- + \oplus$ .

## III. ELECTRICAL TRANSFERENCE

64. **Phenomenon of Electrical Transference.** — When a current is passed through a solution of a salt, base, or acid, in addition to the chemical changes taking place at the electrodes in accordance with Faraday's law, a certain quantity of the cation-constituent is transferred from the neighborhood of the anode to that of the cathode, and a certain quantity of the anion-constituent is transferred in the reverse direction. This phenomenon can best be made clear by the consideration of an actual transference determination. Consider, for example, that a 0.02 normal solution of sodium sulfate is electrolyzed at 18° in



an apparatus like that shown in the figure, between a platinum cathode (marked -) and a platinum anode (marked +). To avoid stirring of the solution, the electrodes, from which hydrogen and oxygen gases are evolved, are placed near the surface; the anode, around which the solution becomes denser during the electrolysis, is placed near the bottom of the tube; and the apparatus is immersed in a water-bath kept at constant temperature. The current is stopped before the hydroxide-ion produced at the cathode and the hydrogen-ion produced at the anode have been transferred beyond the dotted lines in the figure. The three portions of the solution (called the cathode-portion, middle-portion, and anode-portion, and marked C, M, and A,

respectively) are then separately removed from the apparatus, and submitted to analysis. The quantity of sodium and of sulfate present in each portion is compared with the quantity of it originally associated with the weight of water contained in the portion. It is found, if the experiment has been successful, that the middle-portion has undergone no change in composition, that the cathode-portion has increased its sodium-content and decreased its sulfate-content, and that the anode-portion has increased its sulfate-content and decreased its sodium-content. It is found, per faraday of electricity passed through the solution, that the sodium-content has increased in the cathode-portion by 0.39 equivalent and has decreased in the anode-portion by the same amount, and that the sulfate-content has in-

creased in the anode-portion by 0.61 equivalent and has decreased in the cathode-portion by the same amount.

*Prob. 9. — The Resultant Effects of Transference and Electrolysis. —*

*a.* Write electrochemical equations expressing the changes produced by the electrolysis at each electrode in the experiment with sodium sulfate described above, and tabulate the number of equivalents of each ion-constituent produced per faraday by the electrolysis both in the cathode-portion and the anode-portion. *b.* Tabulate also the gain and loss caused by the transference per faraday in the number of equivalents of each ion-constituent in the cathode-portion and in the anode-portion. *c.* Tabulate the resultant effect of the electrolysis and transference on the gain and loss in the number of equivalents of sodium sulfate, sodium hydroxide, and sulfuric acid in the cathode-portion and in the anode-portion.

When either of the constituents whose transference is being determined is deposited on or dissolved off the electrode, as is the case when a silver nitrate solution is electrolyzed between silver electrodes, the quantity of it so deposited or dissolved must evidently be determined either by direct weighing or by calculation with the aid of Faraday's law, and be subtracted from or added to the change in content of that constituent in the electrode portion.

**65. Law of Transference.** — The sum of the number of equivalents of the cation and anion constituents ( $N_C$  and  $N_A$ ) transferred in the two directions is equal to the number of faradays ( $N$ ) passed through the solution. That is,  $N_C + N_A = N$ . This law, called the *law of transference*, supplementing Faraday's law of electrolysis, is illustrated by the data for sodium sulfate given above.

In the case of mixtures containing various ion-constituents ( $C_1, C_2, \dots, A_1, A_2, \dots$ ) all of these are transferred, and the expression of the law of transference is:  $N_{C_1} + N_{C_2} \dots + N_{A_1} + N_{A_2} \dots = N$ .

**66. Transference-Numbers.** — The equivalents  $N_C$  of cation-constituent transferred are in general not equal to the equivalents  $N_A$  of anion-constituent transferred. The experimentally determined number of equivalents of any ion-constituent transferred per faraday of electricity, whether in a solution of a single salt or a mixture of salts, is called the *transference-number*  $\tau$  of that constituent. Thus in the case of sodium sulfate  $\tau_{Na} = 0.39$  and  $\tau_{SO_4} = 0.61$ . In accordance with the law of transference the sum of the transference-numbers of all the ion-constituents is equal to unity.

*Determination of Transference-Numbers. —*

*Prob. 10.*—Through a 0.1 formal solution of potassium sulfate between platinum electrodes 0.0075 faraday is passed at 25°. The cathode-portion after the electrolysis is found to contain 0.1450 g. more potassium than was originally associated with the weight of water in the portion. Calculate the transference-number of the sulfate-ion.

*Prob. 11.*—A current is passed at 25° through a solution of 16.64 g. of  $\text{Pb}(\text{NO}_3)_2$  in 1000 g. of water between lead electrodes until 0.1658 g. of silver is deposited in a coulometer in series with it. The anode portion weighed 62.50 g. and yielded on analysis 1.123 g. of  $\text{PbCrO}_4$ . Calculate the transference-number of the lead-ion. Assume that lead dissolves off the anode in accordance with Faraday's law. *Ans.* 0.489.

**67. The Mechanism of Conduction in Solutions.**—Just as Faraday's law shows that electricity is carried from the solution to the electrode only by the ion-constituents, so the law of transference shows that through the solution the electricity is likewise carried only by the ion-constituents. The only difference is that often only one kind of ion-constituent carries the electricity to the electrode, while all the ion-constituents present take part in the conduction of it through the solution.

That the ion-constituents do move through the solution can be shown by placing the solution of a salt, such as copper sulfate or potassium permanganate, whose cation or anion has a characteristic color, beneath a solution of a colorless salt, such as potassium sulfate, and applying a potential-difference at the electrodes.

The movement of the ion-constituents is explained by the ionic theory as follows. A certain fraction of the molecules of a salt exists in the state of positively and negatively charged molecules—the cations and anions. When a solution is placed between electrodes that are at different potentials, the ions in virtue of their charges are subjected to an electric force which drives them through the solution—the cations towards the cathode, the anions towards the anode; while the unionized molecules, being electrically neutral, are unaffected. The ions are, however, constantly uniting to form unionized molecules, and the latter are constantly dissociating into ions. For this reason although at any moment only the ions are moving the resultant effect is that the ion-constituent as a whole moves continuously towards the electrode. The rate at which the ion-constituent moves is equal to the rate at which the ion moves multiplied by the ionization of the salt; for the statement that a certain fraction

of the molecules is ionized is equivalent to the statement that any one molecule exists in the form of its ions during that fraction of the time. The quantitative application of these considerations to transference is discussed in the following article.

**68. Transference in Relation to the Mobility of the Ions.** — The electric force  $f$  acting on any charged body is equal to its charge  $Q$  multiplied by the potential-gradient; that is,  $f = Q (dE/dl)$ , where  $dE$  is the change of potential in the distance  $dl$ . Moreover, the velocity of any body moving through a medium of great frictional resistance is proportional to the force acting upon it. Therefore, since the resistance to the motion of ions through solutions is very great, the velocity  $u$  of any given ion is proportional to the potential-gradient; that is:  $u = v (dE/dl)$ , where  $v$  is the velocity under unit potential-gradient, called the *mobility of the ion*. The velocity of the ion-constituent is evidently also proportional to the potential-gradient; and its velocity under unit potential-gradient is called the *mobility of the ion-constituent*.

As shown in the following problem, the ratio of the mobilities of the two constituents is equal to the ratio of the transference-numbers, and the fraction of the current carried by each constituent is equal to its transference-number.

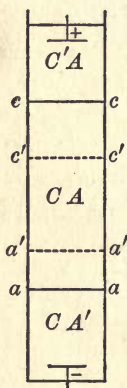
**Prob. 12. — Transference in Relation to Ion-Mobility.** — A 0.1 normal solution of NaCl at 18° is placed in a vertical cylindrical tube 2 cm. in diameter between electrodes 20 cm. apart. At the upper electrode a potential-difference of 50 volts is applied, and the concentration changes at the electrodes are eliminated so that the potential-gradient remains uniform throughout the tube. The mobilities of the sodium and chloride ion-constituents in this solution at 18° have been found to be 0.000373 and 0.000578 cm. per second, respectively. *a.* Sketch the apparatus approximately to scale. Calculate the distance which each of the ion-constituents moves in 30 minutes, and locate these distances in the sketch with reference to a cross-section indicated in the middle part of the tube. *b.* Calculate the number of equivalents of each ion-constituent transferred through any cross-section in 30 minutes. *c.* Calculate the transference-numbers of the two ion-constituents, and show that the ratio of them is equal to the ratio of their mobilities. *d.* Calculate the current due to the migration of each ion-constituent, and show that its transference-number is equal to the fraction of the current carried by it. *Ans. b, 0.000527 equivalent of Na.*

**Prob. 13. — Derivation of the Mobility of Ion-Constituents from Transference Experiments.** — An ordinary transference determination is made at 18° with 0.1 normal AgNO<sub>3</sub> solution in a vertical tube 4 cm. in

diameter between silver electrodes 30 ccm. apart. Analysis of the anode-portion, which is withdrawn at the bottom, shows that 0.00207 equivalent of silver has migrated out of it. *a.* Sketch the apparatus, indicating a boundary of the anode-portion and a boundary of a region above it which contains all the silver which was transferred out of the anode portion. *b.* Calculate the distance through which the silver migrated during the passage of the current, referring to the sketch for the relations involved. *c.* The potential-difference applied at the electrodes was 10 volts, and the concentration changes at the electrodes were eliminated so that the potential-gradient was uniform. The resulting current of 0.0395 ampere passed for 3 hours. Calculate the mobility in centimeters per second of each of the ion-constituents. *Ans. c.* 0.000520 for the  $\text{NO}_3$ .

**69. The Moving-Boundary Method of Determining Transference.** —

A direct method of determining transference-numbers is based on the proportionality between ion-mobility and transference considered



in Art. 68. In this method, which is illustrated by the figure, the relative rates are measured at which the two boundaries of a solution of a salt  $\text{CA}$  move when placed between solutions of two other salts  $\text{C}'\text{A}$  and  $\text{CA}'$ , arranged as in the figure, in which  $cc$  and  $aa$  represent the original positions of the boundaries,  $c'c'$  and  $a'a'$  their positions after a certain time. It is evident that the cation-constituent  $\text{C}$  moves the distance  $cc'$  while the anion-constituent  $\text{A}$  moves the distance  $aa'$ ; and that they are moving under the same potential-gradient, since they are in the same solution. Therefore the ratio  $cc'/aa'$  is the ratio of the mobilities  $u_c/u_a$ , and hence of the transference-numbers  $T_c/T_a$ .

The boundaries are most readily seen when the "indicator" ions  $\text{C}'$  and  $\text{A}'$  are colored; but even when the ions are all colorless, the boundaries are usually visible because of the different refractive power of the adjoining solutions.

*Prob. 14. — Experimental Determination of Transference-Numbers by the Moving-Boundary Method.* — In a moving-boundary experiment an apparatus like that represented in the figure is charged at  $18^\circ$  with solutions of silver nitrate at the bottom, of potassium nitrate in the middle, and of potassium acetate at the top. The lower electrode, which is of silver, is made the anode. In 90 minutes the lower boundary moves 3.00 cm. and the upper boundary 2.88 cm. Sketch the apparatus, indicating the positions of the three solutions and the boundaries between them at the beginning and end of the experiment. State what transference-numbers can be derived, and calculate their values.

\*In order that the boundary between the two solutions C'A and CA remain sharp, it is essential that the ion C' have a smaller mobility than the ion C which precedes it. For evidently, if any quantity of this ion C', through migration or convection, should enter the solution CA, it would in consequence of its lesser mobility move in that solution with a smaller velocity than the ion C and drop back to the boundary. That the ion C' does not, as a result of its smaller mobility, lag behind and thus destroy the sharpness of the boundary, is due to the facts that, when it begins to do so, its concentration in the region behind the boundary decreases, and consequently the resistance of the solution and therefore the potential-gradient in that region increases, which in turn increases the actual velocity of the ion and brings it back to the boundary. It can be shown (as in Prob. 38, Art. 80) with the aid of the principles correlating resistance with concentration and ion-mobilities (considered in Art. 73) that the concentration of the substance C'A automatically adjusts itself so that the ratio of this concentration to that of the substance CA is equal to the ratio of the transference number of the ion-constituent C' in the solution C'A to that of the ion-constituent C in the solution CA.

**70. Change of Transference-Numbers with the Concentration.** — The following table shows the transference-numbers of some typical substances at 18° at a series of concentrations.

TRANSFERENCE-NUMBERS AT VARIOUS CONCENTRATIONS

<i>Equivalent per liter</i>	<i>Anion Transference-Numbers</i>		
	<i>KCl</i>	<i>HCl</i>	<i>NaCl</i>
0.00	0.504	0.172	0.602
0.01	0.504	0.167	0.604
0.05	0.504	0.166	0.605
0.10	0.505	0.165	0.607
0.20	0.506	0.163	0.610
1.00	—	0.156	0.631

It will be noticed that the transference-number in the case of potassium chloride does not change appreciably with decreasing concentration below 0.1 normal. It is therefore to be inferred that the transference-number will have this same value (0.504) as the concentration approaches zero, as shown in the table. The value at zero concentration evidently corresponds in general to a definite ratio of the mobilities of the ions in pure water; and an accurate knowledge

of one such value is of importance, since it enables the conductances of all the various ions to be evaluated, as will be shown in Art. 76. The transference-numbers given in the table for sodium chloride and hydrochloric acid at zero concentration are not the results of transference measurements, but were derived conversely from the conductances of the separate ions.

The transference-numbers for sodium chloride and hydrochloric acid change considerably with the concentration even below 0.2 normal. Thus the change in the transference-numbers in passing from 0.2 normal to 0.0 normal corresponds to a change in the ratio of the mobilities of the chloride and sodium ions from 1.56 to 1.51 (or 3.2%) and in the ratio of the mobilities of the hydrogen and chloride ions from 5.14 to 4.81 (or 6.4%). This change in the relative mobilities of the two ions has an important bearing, considered in Art. 74, on the change of conductance with the concentration; for it shows that a change in the actual mobility of some of the ions takes place even at these low concentrations. Thus, if the chloride ion has the same mobility at the concentrations 0.2 and 0.01 normal, the sodium ion must have a 3.2% smaller mobility in the 0.2 normal solution; but the chloride ion also may well have a smaller mobility at 0.2 than at 0.01 normal, in which case the mobility of the sodium ion would decrease by even more than 3.2%.

At concentrations above 0.2 normal the transference-number often changes rapidly with increasing concentration. This may be due to a variety of influences not affecting the values at smaller concentrations. Thus it may arise from a change in the frictional resistance of the medium; from hydration of the ions, which causes water to be transferred and thus affects the transference value, since this is computed under the assumption that the water is stationary; from existence of intermediate ions or complex ions, which in concentrated solutions are more likely to be present in considerable quantity.

**71. The Composition of Ions Determined by Transference Experiments.** — Transference experiments furnish in many cases useful information as to the nature of the ions present in the solution. Thus they may show, as illustrated by the following problems, the formation of complex cations or anions and the existence of hydrated ions. They may also indicate the extent to which salts are hydrolyzed in solution.

*Formation of Complex Ions. —*

*Prob. 15.* — When a current is passed through a solution of potassium silver cyanide ( $\text{KCN}.\text{AgCN}$ ) silver deposits on the cathode and the cathode-portion loses 1.40 equivalents of silver and 0.80 equivalent of cyanogen, and gains 0.60 equivalent of potassium per faraday. *a.* Explain what this shows in regard to the composition of the ions and their transference-numbers. *b.* Write an electrochemical equation showing the substances actually produced and destroyed.

*Prob. 16.* — A transference experiment is made by passing 0.01 faraday through a solution 0.2 formal in  $\text{AgNO}_3$  and 0.6 formal in  $\text{NH}_3$  between silver electrodes at  $18^\circ$ . The anode-portion is found to gain 0.0053 equivalent of silver and to lose 0.0094 formula-weight of  $\text{NH}_3$ . Explain what this shows in regard to the composition of the ions. (Silver dissolves at the anode in accordance with Faraday's law.)

*\*Prob. 17. — The Hydration of Ions.* — In a transference experiment 0.0629 faraday was passed at  $25^\circ$  through a solution placed between a silver anode and a silver cathode coated with silver chloride and containing 1.21 formula-weights of  $\text{NaCl}$  and 0.1 formula-weight of raffinose ( $\text{C}_{18}\text{H}_{32}\text{O}_{16}$ ) in 1000 g. of water. The anode-portion was found by analysis to contain 0.96 g. less water and 1.41 g. less  $\text{NaCl}$  than was originally associated with the raffinose present in that portion. *a.* Calculate the number of mols of water and the number of equivalents of sodium transferred per faraday from the anode to the cathode, assuming that the raffinose does not migrate. *b.* Assuming no hydration of the chloride ion, calculate the number of molecules of water associated with the atom of sodium in the sodium ion. *c.* Assuming the chloride ion to be hydrated with  $x$  molecules of water, derive an expression for the hydration of the sodium ion. *Ans. c,  $2.0 + 1.61 x$ .*

Transference experiments, like that described in the preceding problem, have been made with various other chlorides for the purpose of determining the hydration of the ions. These experiments have led to the following mean values for the number of molecules of water contained in other ions, assuming the number in the chloride ion to be  $x$  molecules:

$$\text{H}^+ : 0.28 + 0.185 x.$$

$$\text{Cs}^+ : 0.67 + 1.03 x.$$

$$\text{K}^+ : 1.3 + 1.02 x.$$

$$\text{Na}^+ : 2.0 + 1.61 x.$$

$$\text{Li}^+ : 4.7 + 2.29 x.$$

## IV. ELECTRICAL CONDUCTANCE

**72. Conductance, Specific Conductance, and Equivalent Conductance.** — According to *Ohm's law*, the current  $I$  flowing between two planes of a conductor is proportional to the potential-difference  $E$  at those planes. The ratio of the current to the potential-difference is called the *conductance*  $L$ ; and the inverse ratio, the *resistance*  $R$ . That is,

$$I/E = L, \text{ and } E/I = R.$$

When the current is expressed in amperes and the potential-difference in volts, the resistance is in ohms and the conductance in reciprocal ohms. An *ohm* is the resistance, and a *reciprocal ohm* (or *mho*) the conductance, of a column of mercury at  $0^\circ$  one square millimeter in cross-section and 106.3 centimeters long.

In accordance with these definitions, the conductance, expressed in reciprocal ohms, of any conductor is the number of coulombs which pass per second when the potential-difference at the ends is one volt.

The conductance of a homogeneous body of uniform cross-section is proportional to its cross-section  $a$  and inversely proportional to its length  $l$ . That is,  $L = \bar{L} a/l$ . The proportionality-factor  $\bar{L}$ , which is the conductance when the cross-section is one square centimeter and the length one centimeter, is called the *specific conductance*. Its reciprocal is called the *specific resistance*.

It has been shown by transference measurements and by other considerations that in aqueous solutions of salts, acids, and bases, the ions of the water are present at a concentration which is negligible even when the concentration of the ions of the solute is as small as 0.0001 normal. The conductance of such solutions therefore arises only from the motion of the ions of the salt, acid, or base; and it is convenient to employ a concept by which the conductance may be referred to one equivalent of the solute. Such a concept is *equivalent conductance*  $\Lambda$ , which is defined to be the conductance of that volume of solution which contains one equivalent of salt, acid, or base, when placed between parallel electrodes one centimeter apart. Since the equivalent conductance varies with the volume of the solution in which the equivalent of salt is dissolved, it is necessary to specify the normal concentration to which any given value refers. Thus, in accordance with these statements, the equivalent conductance  $\Lambda_{0.1}$  of a salt in 0.1 normal solution denotes the conductance of 10,000 cubic centi-

meters of that solution when placed between parallel electrodes one centimeter apart.

*Relations between Conductance, Specific Conductance, and Equivalent Conductance.* —

*Prob. 18.* — Find the specific conductance in reciprocal ohms of mercury at  $0^{\circ}$ .

*Prob. 19.* — *a.* Derive an algebraic relation expressing equivalent conductance in terms of specific conductance and of concentration in equivalents per cubic centimeter. *b.* Calculate the specific conductances of 0.1 and 0.01 normal NaCl solutions whose equivalent conductances at  $18^{\circ}$  are 92.0 and 101.9 reciprocal ohms, respectively.

*Prob. 20.* — A 0.1 normal  $\text{AgNO}_3$  solution at  $18^{\circ}$  is placed in a tube 4 cm. in diameter between silver electrodes 12 cm. apart. A potential difference of 20 volts at the electrodes produces a current of 0.1976 ampere. Calculate the conductance, the specific conductance, and the equivalent conductance of the solution.

*Prob. 21.* — The equivalent conductance of a 0.01 normal  $\text{CuSO}_4$  solution at  $18^{\circ}$  is 71.7 reciprocal ohms. Calculate the resistance of a column of it 20 cm. long and 5 sqcm. in cross-section.

*Prob. 22.* — *Experimental Determination of Specific Conductance.* — In a cylindrical vessel with fixed platinum electrodes are measured in succession the resistances at  $18^{\circ}$  of a 0.01 normal KCl solution, a 0.001 normal  $\text{K}_2\text{SO}_4$  solution, and the distilled water used for preparing these solutions (which has an appreciable conductance due to impurities, such as carbonic acid and ammonium hydroxide). These resistances are found to be 97.8, 937, and 100,000 ohms, respectively. *a.* Find the conductances in the vessel of the two solutions and of the water; also the conductances which the two solutions would have shown if the water had been free from the impurities (which do not react chemically with the neutral salts). *b.* From these results and the specific conductance at  $18^{\circ}$  of pure 0.01 normal KCl solution, which is known to be 0.001225 reciprocal ohm, calculate the specific conductance of pure 0.001 normal  $\text{K}_2\text{SO}_4$  solution. *Ans. b, 0.0001268.*

**73. Conductance in Relation to the Mobility of the Ion-Constituents.** — The discussion of the mechanism of conduction in solutions in Arts. 67 and 68, considered in connection with the definition of equivalent conductance given in Art. 72, leads to the following principles, which are further illustrated by the problems below.

(1) The equivalent conductance of a substance at any concentration is the sum of the equivalent conductances of the ion-constituents at that concentration; and the transference-number of an ion-constituent is the ratio of its equivalent conductance to the sum of the equivalent conductances of the two ion-constituents. That is,

$$L = \sum v L_i$$

$$v = \frac{L_i}{L}$$

$\Lambda_c = \Lambda_c + \Lambda_a$ ,  $T_c = \frac{\Lambda_c}{\Lambda_c + \Lambda_a}$  or  $T_a = \frac{\Lambda_a}{\Lambda_c + \Lambda_a}$ , where  $\Lambda_c$  and  $\Lambda_a$  are the equivalent conductances of the cation and anion constituents at any definite concentration.

(2) The equivalent conductance of an ion-constituent in any solution is equal to the product of its mobility  $u$  in that solution by the charge  $F$  on one equivalent; that is,  $\Lambda_c = u_c F$ , and  $\Lambda_a = u_a F$ .

*Prob. 23. — Equivalent Conductance in Relation to the Mobilities of the Ion-Constituents. —* Derive principle (2) stated above by considering the number of equivalents of each constituent that reaches the electrode per second in an apparatus corresponding to the definition of equivalent conductance.

*Prob. 24. — Specific Conductance in Relation to the Concentrations and Mobilities of the Ion-Constituents. —* Derive an expression for the specific conductance  $\bar{\kappa}$  of a solution containing KCl at concentration  $c_1$  and NaNO<sub>3</sub> at concentration  $c_2$  by considering the number of equivalents of each constituent that reach the electrodes per second in an apparatus corresponding to the definition of specific conductance.

**74. Change of Equivalent Conductance with the Concentration. —** The effect of the concentration on the equivalent conductance of various types of substances is illustrated by the following table.

EQUIVALENT CONDUCTANCE AT 18°				
Equivalents per liter	NaCl	K <sub>2</sub> SO <sub>4</sub>	HCl	HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>
1.0	74.3	71.6	—	1.34
0.1	92.0	94.9	351.4	4.68
0.01	101.9	115.8	369.3	14.5
0.001	106.4	126.9	375.9	—
0.0001	108.0	130.7	378.1	—
0.0	108.5	132.0	378.3	348.

The equivalent conductance is seen in all cases to increase with decreasing concentration, and in the case of the first three (largely ionized) substances to approach at the lower concentrations a constant limiting value. This limiting value, which by definition is the value approached by the conductance of one equivalent of substance between electrodes one centimeter apart as the volume in which it is dissolved approaches infinity, is called the *equivalent conductance at zero concentration*, and is denoted by  $\Lambda_0$ . This value corresponds to complete ionization, as will be shown later.

In the case of largely ionized substances, the  $\Lambda_0$  value is obtained by extrapolation from the values measured at concentrations between

0.1 and 0.0001 normal. In the case of substances (such as acetic acid) that are not largely ionized, the equivalent conductance is far removed from the limiting value corresponding to complete ionization, even at the lowest concentration at which accurate measurements can be made. For such substances the  $\Lambda_0$  value cannot be directly derived, but is obtained with the aid of the principles that the equivalent conductance of a substance is the sum of the equivalent conductances of its ion-constituents, and that at zero concentration any definite ion-constituent has the same conductance whatever be the other ion-constituent with which it is associated. This last principle is a consequence of the facts that at zero concentration the ion-constituents are present wholly in the form of the (free) ions, and move through the same medium (pure water), whatever be the substance from which they originate.

*Prob. 25. — Derivation of  $\Lambda_0$  Values for Slightly Ionized Substances. —*  
*a.* Derive the  $\Lambda_0$  value at 18° for  $\text{HC}_2\text{H}_3\text{O}_2$  from the above stated principles and the following data. The  $\Lambda_0$  values for  $\text{HCl}$ ,  $\text{NaCl}$ , and  $\text{NaC}_2\text{H}_3\text{O}_2$  derived by direct extrapolation from observed data are 378.3, 108.5, and 78.2 respectively. *b.* State what  $\Lambda_0$  values obtainable by extrapolation might be used to derive the  $\Lambda_0$  value for  $\text{NH}_4\text{OH}$ , a slightly ionized substance.

The conductance of slightly ionized substances (such as acetic acid) changes with the concentration in the way that the mass-action law requires, assuming that the conductance is proportional to the ionization, as will be considered in Art. 75. But this is not even approximately true of the conductance of largely ionized substances (like sodium chloride, hydrochloric acid, and potassium sulfate). In the case of these substances, the fractional decrease of the equivalent conductance is closely proportional to the cube-root of the concentration for uniunivalent salts between 0.001 and 0.2 normal, and somewhat less accurately so for unibivalent salts between 0.001 and 0.1 normal. This empirical principle is expressed by the equations:

$$\frac{\Lambda_0 - \Lambda}{\Lambda_0} = B c^{\frac{1}{3}}; \text{ or } \Lambda = \Lambda_0 (1 - B c^{\frac{1}{3}}).$$

In these equations  $B$  is a constant for any definite substance at a definite temperature. Its value is not greatly different for different salts of the same valence type, and it varies only slightly with the temperature. Thus at 18° or 25° its value varies only between 0.30 and 0.45 for uniunivalent salts, and between 0.50 and 0.75 for unibivalent salts. For largely ionized uniunivalent acids and bases the

value is somewhat smaller than for the neutral salts; thus for hydrochloric acid it is 0.17. This equation is approximately true for any definite substance also when other largely ionized substances are present with it in the solution, the concentration  $c$  then denoting the sum of the normal concentrations of all the substances.

*\*Prob. 26. — a.* Plot the values of the equivalent conductance of sodium chloride and of potassium sulfate given in the above table as ordinates against the cube-root of the concentration as abscissas, including also the  $\Lambda$  values at 0.2 normal, which are 87.7 for NaCl and 87.7 for  $K_2SO_4$ ; and draw a smooth curve through the points. *b.* By extending the straight-line portion of the graph find the values of  $\Lambda_0$  and of the constant  $B$  to which the cube-root equation leads. (The value of  $\Lambda_0$  occurring in the cube-root equation is slightly larger (about 1% for uniunivalent salts) than that obtained by extrapolating with the aid of functions which correspond more closely to the observed conductance values at concentrations between 0.001 and 0.001 normal. The cube-root equation seems to become inexact at these very small concentrations).

The specific conductance of mixtures of largely ionized substances has been found to be determined by the principle that each of the substances has approximately that equivalent conductance which it would have if it were present alone in the solution at a normal concentration equal to the sum of the normal concentrations of all the substances present. With the aid of this principle the specific conductance of such mixtures can be calculated; it being noted that each substance contributes to the specific conductance an amount equal to the product of its equivalent conductance in the mixture by its normal concentration.

*Specific Conductance of Mixtures of Largely Ionized Substances. —*

*Prob. 27. —* Find the specific conductance at 18° of a solution 0.08 normal in NaCl and 0.02 normal in HCl, referring to the above table of conductances for the data needed.

*\*Prob. 28. —* Find the specific conductance at 18° of a solution 0.10 normal in  $K_2SO_4$  and 0.05 normal in NaCl, with the aid of the plot made in Prob. 26.

**75. Conductance in Relation to the Concentration and Mobility of the Ions. —** The relation of conductance to the mobility of the *ion-constituents* was considered in Art. 73. It remains to consider its relation to the concentration and mobilities of the *ions*; for it is the motion of the ions themselves which really constitutes the mechanism of conduction.

It has already been explained in Art. 67 that the mobility  $u_c$  or  $u_a$  of an ion-constituent at any definite concentration  $c$  is equal to the mobility  $u_{c+}$  or  $u_{a-}$  of the (free) ion at that concentration multiplied by the ionization  $\gamma$  of the substance; that is,  $u_c = \gamma u_{c+}$  and  $u_a = \gamma u_{a-}$ . Combining this principle with the principles (Art. 73) that the equivalent conductance of an ion-constituent at any definite concentration is the product of its mobility by the charge  $F$  on one equivalent, and that the equivalent conductance of a substance at any definite concentration is the sum of the equivalent conductances of its ion-constituents at that concentration, the following algebraic expression for the equivalent conductance  $\Lambda$  of a substance is obtained:

$$\Lambda = \gamma u_{c+} F + \gamma u_{a-} F. \quad (1)$$

For the specific conductance the corresponding expression is:

$$\bar{L} = c \gamma u_{c+} F + c \gamma u_{a-} F. \quad (2)$$

These equations express the fundamental factors determining conductance. These factors are: (1) the number of equivalents of (free) cations and anions (the carriers of the electricity) between the electrodes; (2) the mobilities of these ions (that is, their velocities under a potential-gradient of one volt per centimeter), and (3) the quantity of electricity (96,500 coulombs) carried by each equivalent of ions.

Any variation in the equivalent conductance of any definite substance must therefore be due to a change either in the number of ions resulting from the ionization of the substance or in the mobilities of its ions; or to both these effects. Thus, since the limiting value  $\Lambda_0$  of the equivalent conductance approached as the concentration approaches zero obviously corresponds to complete ionization of the substance and to the mobility of its ions in pure water, the smaller values of  $\Lambda$  observed at larger concentrations must arise from a decrease either in the ionization or in the mobility of the ions or from changes in both of these quantities. In other words, the ratio of the equivalent conductance at any concentration to that at zero concentration, hereafter called simply the *conductance-ratio*, is expressed in terms of the fundamental factors determining conduction by the following equation:

$$\frac{\Lambda}{\Lambda_0} = \gamma \frac{u_{c+} + u_{a-}}{(u_{c+})_0 + (u_{a-})_0}. \quad (3)$$

This relation presupposes that the nature of the ions does not change with increasing concentration; thus the conductance-ratio

would not be determined solely by the ionization of  $\text{H}_2\text{SO}_4$  into  $\text{H}^+$  and  $\text{SO}_4$  ions and by the mobilities of these ions, if an appreciable proportion of  $\text{HSO}_4^-$  ions were present at the larger concentrations. In such a case, the conductance-ratio would have no simple significance.

So long as the solution is so dilute that it does not differ appreciably from pure water as a medium offering frictional resistance to the motion of the ions, the mobility of the ions may be expected to remain constant. In that case, and provided that only the same kinds of ions are present at the higher concentration as in the very dilute solution, the conductance-ratio is equal to the ionization; that is:

$$\frac{\Lambda}{\Lambda_0} = \gamma. \quad (4)$$

This principle may be employed for determining the ionization of slightly and moderately ionized substances up to concentrations such as 0.1 to 0.2 normal.

*Prob. 29. — Determination of Ionization from the Conductance-Ratio. —* From the data given in the table of Art. 74, calculate the ionization of acetic acid at  $18^\circ$  in 0.1 and 0.01 normal solutions.

In moderately concentrated solutions the frictional resistance to the motion of the ions must be appreciably different from that in pure water; and the conductance-ratio  $\Lambda/\Lambda_0$  cannot therefore be an exact measure of the ionization. An approximate estimate of the variation of this frictional resistance is given by the ratio of the viscosity  $\eta$  of the solution to the viscosity  $\eta_0$  of pure water at the same temperature. This viscosity-ratio  $\eta/\eta_0$  is determined by measuring the relative times required for equal volumes of the solution and of pure water to flow through the same capillary tube, when subjected to the same pressure. A film of the liquid adheres firmly to the walls of the tube; and the phenomenon of the flow consists essentially in the slipping of the successive cylindrical shells of liquid past one another. Viscosity is therefore a property which depends on the frictional resistance to the motion of the molecules of the liquid past one another; and it may be expected to be roughly proportional to the frictional resistance to the motion of the ions through the same solution. The mobilities of the ions would then decrease in the same proportion as the viscosity of the solution increases; that is:

$$\frac{u_{\text{C}^+} + u_{\text{A}^-}}{(u_{\text{C}^+})_0 + (u_{\text{A}^-})_0} = \frac{\eta_0}{\eta}. \quad (5)$$

By substituting this viscosity-ratio for the ratio of the mobilities of

the ions in the general expression for the conductance-ratio (equation (3), there results the relation

$$\gamma = \frac{\Lambda \eta}{\Lambda_0 \eta_0} \quad (6)$$

That is, in case the viscosity is the only influence affecting the mobilities, as seems to be approximately true as long as the concentration of ions in the solution is small (not greater than about 0.01 normal), the ionization is approximately equal to the *conductance-viscosity ratio*. This ratio therefore serves to determine the ionization of slightly ionized substances up to fairly large concentrations

*Prob. 30. — Determination of Ionization from the Conductance-Viscosity Ratio.* — Calculate the ionization of acetic acid in 1 normal solution from the conductance values given in the table of Art. 74 and from the fact that the viscosity of 1 normal acetic acid solution at 18° is 1.113 times as great as that of pure water.

The viscosity correction may be large also in the case of salt solutions, as is shown by the following values of the viscosity-ratio at 18° and 1 normal.

Salt	KCl	LiCl	MgCl <sub>2</sub>	K <sub>2</sub> SO <sub>4</sub>	MgSO <sub>4</sub>
$\eta/\eta_0$	0.982	1.150	1.213	1.101	1.381

The deviation of the ratio from unity at smaller concentrations is approximately proportional to the concentration; thus at 0.1 normal it is about one tenth of that at 1 normal.

In the case of salts, however, this influence of viscosity is superposed on another influence on the mobility of the ions which seems to be large at small ion-concentrations (even at 0.01 normal). Direct evidence that there is such an influence is afforded by the change in transference-numbers at small concentrations (below 0.2 normal) discussed in Art. 70. This influence makes the conductance-ratio an uncertain measure of the ionization of largely ionized substances, even at small concentrations. The ionization of such substances is considered in detail in Art. 79.

**76. Conductance of the Separate Ion-Constituents.** — Since the equivalent conductance of a substance at any definite concentration is the sum of the equivalent conductances of its ion-constituents, and since the transference-number of either ion-constituent is the ratio of its conductance to the total conductance (Art. 73), the equivalent conductance of either ion-constituent at that concentration is obtained

by multiplying its transference-number by the equivalent conductance of the salt.

The equivalent conductance of ion-constituents derived in this way increases with decreasing concentration, and approaches a limiting value as the concentration approaches zero, which is the same whatever be the other ion-constituent which is present with it. This limiting value is the equivalent conductance of the ion itself in pure water, hereafter called simply the *ion-conductance*.

The ion-conductances for the various ions have been derived, as illustrated by the following problem, by the additivity principle from the equivalent conductances of their salts at zero concentration with the aid of a single transference-number, that for potassium chloride, which is the one best known at small concentrations.

*Prob. 31. — Determination of Ion-Conductances. — a.* Calculate the ion-conductances of the potassium and chloride ions at  $18^\circ$  from the transference values given in Art. 70 and from the value 129.6 of the equivalent conductance at zero concentration of potassium chloride. *b.* Calculate the ion-conductances of the sodium, hydrogen, and sulfate ions at  $18^\circ$  from the conductance values in the table in Art. 74.

The following table contains the values of the ion-conductances for some important ions at  $18^\circ$  and  $25^\circ$ .

VALUES OF THE ION-CONDUCTANCES

Cations	$18^\circ$	$25^\circ$	Anions	$18^\circ$	$25^\circ$
H <sup>+</sup>	313.	347.	OH <sup>-</sup>	173.	195.
Li <sup>+</sup>	33.1	39.3	F <sup>-</sup>	46.6	54.3
Na <sup>+</sup>	43.2	50.6	Cl <sup>-</sup>	65.3	75.2
K <sup>+</sup>	64.3	74.2	Br <sup>-</sup>	67.4	77.5
NH <sub>4</sub> <sup>+</sup>	64.5	74.5	I <sup>-</sup>	66.4	76.3
Rb <sup>+</sup>	67.6	77.6	SCN <sup>-</sup>	56.5	—
Cs <sup>+</sup>	67.6	77.6	NO <sub>3</sub> <sup>-</sup>	61.7	70.6
Ag <sup>+</sup>	53.9	62.6	ClO <sub>3</sub> <sup>-</sup>	54.9	63.2
Tl <sup>+</sup>	65.5	75.3	BrO <sub>3</sub> <sup>-</sup>	47.7	54.9
Mg <sup>++</sup>	45.2	53.3	IO <sub>3</sub> <sup>-</sup>	33.8	39.3
Ca <sup>++</sup>	51.4	60.3	C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> <sup>-</sup>	35.	41.
Ba <sup>++</sup>	54.8	63.9	SO <sub>4</sub> <sup>-</sup>	67.7	78.4
Pb <sup>++</sup>	60.2	72.8	CrO <sub>4</sub> <sup>-</sup>	72	—
Cu <sup>++</sup>	46.	54.	C <sub>2</sub> O <sub>4</sub> <sup>=</sup>	61.	—
Zn <sup>++</sup>	46.	54.			
Cd <sup>++</sup>	46.	54.			

$$m_{Cl_2} = 2(44) + 2(65.3)$$

The ion-conductance always increases rapidly with the temperature; for example, at 18° by about 1.8 percent per degree in the case of the fast-moving hydrogen and hydroxide ions and by 2.1 to 2.6 percent in the case of other ions. This increase of conductance evidently corresponds to an equal percentage increase in the mobility of the ion.

*Prob. 32. — Ion-Conductance in Relation to Atomic Weight and Hydration of the Ions. — a.* From a consideration of the table state the relation that exists between the ion-conductances and the atomic weights of the different elementary ions belonging to the alkali group and to the alkaline-earth group. *b.* State how this relation might be explained by reference to the hydration of the ions described at the end of Art. 71.

From these ion-conductances the  $\Lambda_0$  value for the various salts can be obtained by simple addition. This fact is of especial importance in the case of substances for which the  $\Lambda_0$  value cannot be derived from conductance measurements by extrapolation. This is true of weak bases and acids, such as ammonium hydroxide and acetic acid, whose ionization is far from complete even in dilute solution; it is also true of salts, such as ammonium acetate, which are appreciably hydrolyzed in dilute solution.

**77. Determination of the Concentration of Ions and of Largely Ionized Substances by Conductance Measurements.** — Conductance measurements are often employed, both in scientific and technical work, for determining the concentration of the ions in solutions and deriving therefrom the concentration of the largely ionized substances that may be present

When the ion concentration is so small (not greater, for example, than 0.001 normal) that its influence in decreasing the mobilities of the ions can be neglected without serious error, the ion-concentration can be calculated from the measured specific conductance simply with the aid of the ion-conductances (as in Probs. 33 and 34). When the ion-concentration is so large that this influence cannot be neglected, it is first roughly estimated with the aid of the ion-conductances, and the concentration of the substance is then accurately determined by using the known values of the equivalent conductance of the substance in the neighborhood of the estimated concentration (as in Prob. 35).

*Prob. 33. — Determination of the Solubility of Slightly Soluble Substances.* — When water at 18° is saturated with silver chloride, its specific conductance is increased by  $1.25 \times 10^{-6}$  reciprocal ohm. Calculate the solubility of silver chloride in equivalents per liter.

✓ *Prob. 34. — Determination of the Concentration of the Ions in Pure Water.* — The specific conductance of pure water, resulting from its dissociation into  $H^+$  and  $OH^-$  ions, is  $3.8 \times 10^{-8}$  reciprocal ohm at  $18^\circ$ , and  $5.8 \times 10^{-8}$  reciprocal ohm at  $25^\circ$ . Calculate the concentration of the ions in equivalents per liter at each of these temperatures.

✓ *Prob. 35. — Determination of the Hydrolysis of Salts.* — A 0.02 normal  $NH_4CN$  solution has at  $25^\circ$  a specific conductance of 0.00136 reciprocal ohms. This salt is largely hydrolyzed in accordance with the equation  $NH_4CN + H_2O = NH_4OH + HCN$ , and the  $NH_4OH$  and  $HCN$  are so slightly ionized in the presence of their salt as to have only a negligible conductance. The ion-conductances of  $NH_4^+$  and  $CN^-$  at  $25^\circ$  are 74.5 and 70, respectively. Assuming that the equivalent conductance of unhydrolyzed  $NH_4CN$  decreases with the concentration in the same ratio as does that of  $NaCl$  (given in the table of Art. 74) calculate the fraction of the salt that is hydrolyzed. *Ans.* 50%.

## V. THE IONIZATION OF SUBSTANCES

**78. Ionization of Substances Not Largely Ionized.** — As shown in Art. 75, the conductance-ratio or conductance-viscosity ratio can be considered substantially equal to the ionization so long as the total concentration of ions in the solution is small (not greater than about 0.01 normal). The ionization values for many slightly and moderately ionized acids and bases have been determined in this way, with the results stated in the following paragraph.

Acids and bases, unlike salts, exhibit at any moderate concentration, such as 0.1 normal, every possible degree of ionization between a small fraction of one percent and nearly 100 percent. There is, to be sure, a fairly large group of acids and bases, including HCl, HBr, HI, HNO<sub>3</sub>, HClO<sub>3</sub>, KOH, NaOH, LiOH, Ba(OH)<sub>2</sub>, Ca(OH)<sub>2</sub>, which like neutral salts are almost completely ionized. But outside of this group all possible values are met with, as illustrated by the following approximate values of the percentage ionization (100 γ) at 25° and 0.1 normal.

## PERCENTAGE IONIZATION OF ACIDS AND BASES

H <sub>2</sub> SO <sub>3</sub> (into H <sup>+</sup> and HSO <sub>3</sub> <sup>-</sup> ) . . . . .	34%
H <sub>3</sub> PO <sub>4</sub> (into H <sup>+</sup> and H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ) . . . . .	28
HNO <sub>2</sub> and HF . . . . .	8
HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub> and NH <sub>4</sub> OH . . . . .	1 ✓
H <sub>2</sub> S, H <sub>2</sub> CO <sub>3</sub> , and HClO . . . . .	0.1
HCN and HBO <sub>2</sub> . . . . .	0.002

Polybasic acids are known to ionize in stages, giving rise to the intermediate ion; and the first hydrogen is almost always much more dissociated than the second, and the second much more than the third. Thus H<sub>2</sub>SO<sub>3</sub> at 0.1 normal at 25° is about 34 percent dissociated into H<sup>+</sup> and HSO<sub>3</sub><sup>-</sup>, and less than 0.1 per cent dissociated into H<sup>+</sup> and SO<sub>3</sub><sup>=</sup>. Methods by which the dissociation of the successive hydrogens can be determined are referred to in Art. 106.

A few salts of higher valence types form marked exceptions to the principle that salts are almost completely ionized. Thus at 0.1 normal and 25°, the value of the conductance-ratio for cadmium chloride is 0.45 and the values for the mercuric halides are less than 0.001.

**79. Ionization of Largely Ionized Substances.** — There are many facts which indicate that neutral salts and largely ionized univalent

acids and bases, like hydrochloric acid and potassium hydroxide, are completely or almost completely ionized up to moderate concentrations, such as 0.2 normal, and that the decrease in the equivalent conductance of such substances up to these concentrations is therefore due wholly or almost wholly to a decrease in the mobility of the ions. This hypothesis of complete ionization is in contrast with the hypothesis of constant ion-mobility, according to which the decrease in equivalent conductance is wholly or mainly due to a decrease in the ionization of the substance.

The hypothesis of constant ion-mobility, which has ordinarily been employed in the development of the ionic theory, is directly contradicted by the experimental evidence, mentioned in Art. 70, which indicates that the transference-number for certain substances, and therefore the ratio of the mobilities of their two ions, changes considerably with the concentration, even when this is not greater than 0.1 normal.

The hypothesis of constant ion-mobility, moreover, leads to a remarkable uniformity in the ionization-values for substances of the same valence type. Namely, if the conductance-ratio or the conductance-viscosity ratio is regarded as a true measure of ionization, it is necessary to conclude from the facts (stated in Art. 74) in regard to the fractional decrease of equivalent conductance with the concentration that different salts of the same valence type have at any definite concentration nearly equal ionization values. Thus at 18° and 0.1 normal the conductance-viscosity ratio, and under this hypothesis the ionization, has for various salts the following values:

0.852 for NaCl	0.814 for AgNO <sub>3</sub>	0.827 for KClO <sub>3</sub>
0.759 for BaCl <sub>2</sub>	0.731 for Ca(NO <sub>3</sub> ) <sub>2</sub>	0.704 for Na <sub>2</sub> SO <sub>4</sub>

This behavior of salts would indicate that the extent to which their ions in solution combine to form neutral molecules is primarily determined, not by their chemical nature, but only by the magnitude of the charges which they carry. While this is possible, it would signify a new type of chemical combination; for all other chemical reactions are found to depend in a highly specific way on the nature of the atoms and atom-groups uniting with one another, as is the case even in the union of hydrogen-ions with anions to form acids or of hydroxide-ions with cations to form bases.

Another phenomenon, which seems anomalous if the conductance-ratio is regarded as equal to the ionization, is the approximate pro-

portionality between the decrease of this ratio and the cube-root of the concentration, whether the salt be of the uniunivalent type or the unibivalent type; whereas the mass-action law requires (as shown in Art. 103) for either of these types a relation very different from the cube-root function, and moreover, a relation which is a different function for the two valence types.

This divergence which the ionization values derived under the hypothesis of constant ion-mobility show from the requirements of the mass-action law can, to be sure, be explained by assuming that the ions do not behave as perfect solutes and that therefore they exert an abnormal mass-action effect. For, as will be shown in Art. 141, the mass-action law is valid only when the substances involved in the equilibrium to which it is applied (in this case to the equilibrium between the ions and the unionized part of the salt) behave as perfect solutes. Moreover, the ionization values derived from the effect of salts on the molal properties of solutions, such as the vapor-pressure and freezing-point, under the assumption that the ions and unionized molecules are perfect solutes, show that this assumption cannot be correct; for, though these ionization values as a rule agree well with those derived from the conductance, yet like the latter they do not change with the concentration even approximately in accordance with the mass-action law.

The foregoing considerations may be summed up as follows: (1) either hypothesis explains equally well the conduction through solutions; (2) either hypothesis, in order to account for all the facts, must be supplemented by the further hypothesis that the ions are not perfect solutes and therefore have abnormal effects on the molal properties of solutions and an abnormal mass-action in determining equilibrium; (3) the hypothesis of constant ion-mobility leads to improbable consequences in regard to the ionization of largely ionized substances, and requires for the expression of the mass-action of an ion-constituent at each concentration, not only (as does the other hypothesis) a coefficient expressing the deviation of the behavior of the ions from that of perfect solutes, but also an ionization-value expressing their concentration which cannot be determined by any reliable method.

Since in the present state of our knowledge the hypothesis that the ionization of largely ionized substances is substantially complete up to moderate concentrations serves to explain the facts as satisfactorily

as the alternative hypothesis, and since it is simpler in its application, it is employed in the following chapters. In using this principle the possibility must, however, be kept in mind that a more complete study of the properties of largely ionized substances may show that neither of these hypotheses is alone adequate to explain fully their behavior; in other words, it may prove necessary to assume that both the ion-mobilities and the ionization of these substances vary with the concentration.

## VI. APPLICATIONS OF THE LAWS OF CONDUCTANCE AND TRANSFERENCE

## 80. Review Problems.

*Prob. 36.* — *a.* A 0.06 formal solution of  $\text{Cl}_2$  in water in which a partial reaction has taken place according to the equation  $\text{Cl}_2 + \text{H}_2\text{O} = \text{HCl} + \text{HClO}$  has a freezing-point of  $-0.180^\circ$ . Calculate what fraction of the  $\text{Cl}_2$  has undergone change, regarding the  $\text{HClO}$  as unionized and the ions of the  $\text{HCl}$  as perfect solutes. *b.* Calculate the fraction that has undergone change from the following data. The solution has a specific conductance of 0.00472 reciprocal ohm at  $0^\circ$ . The equivalent conductances of  $\text{HCl}$  at  $0^\circ$  between 0.0 and 0.1 normal are 0.700 times those at  $18^\circ$  given in Art. 74. *Ans. a, 0.31.*

*Prob. 37.* — A 0.1 normal solution of chlorplatinic acid,  $\text{H}_2\text{PtCl}_6$ , is electrolyzed at  $25^\circ$ , platinum alone being deposited on the cathode. Assume that this acid dissociates into  $2\text{H}^+$  and  $\text{PtCl}_6^-$  ions, whose equivalent conductances at  $25^\circ$  are 347 and 68, respectively, and that these ions are the only ones present that carry a significant fraction of the current through the solution. *a.* Write the electrochemical equation expressing the cathode process. *b.* Find what changes in the hydrogen, chlorine, and platinum content, expressed in terms of the number of atomic weights of each element, take place in the cathode portion when 4825 coulombs are passed. *Ans. b, loss of 0.0166 at. wt. of Pt.*

*\*Prob. 38.* — From the fact that in a moving-boundary experiment, like that represented in the figure of Art. 69, the ion-constituent  $\text{C}'$  must move in the region behind the boundary with the same actual velocity as the ion-constituent  $\text{C}$  moves in the region beyond the boundary, and from the fact that the respective potential-gradients in these two regions are proportional to the specific resistances there prevailing, show that the ratio of the resulting concentrations of the salts  $\text{C}'\text{A}$  and  $\text{CA}$  in these two regions is equal to the ratio of the transference-number of the ion-constituent  $\text{C}'$  in the solution of  $\text{C}'\text{A}$  to that of the ion-constituent  $\text{C}$  in the solution of  $\text{CA}$ .



## PART II

THE RATE AND EQUILIBRIUM OF CHEMICAL  
CHANGES FROM MASS-ACTION AND  
PHASE VIEW-POINTS

What time would you  
be ready to move  
1.  
2 P.M.  
9

1.3

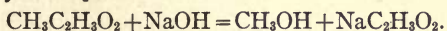
## CHAPTER VI

### THE RATE OF CHEMICAL CHANGES

#### I. THE EFFECT OF CONCENTRATION ON REACTIONS BETWEEN SOLUTES OR GASEOUS SUBSTANCES

**81. Concept of Reaction-rate.** — The *reaction-rate*  $dc/dt$  of a chemical change taking place between dissolved substances may be defined to be the increase  $dc$  either in the weight-normality or in the normal concentration (Art. 35) of the reaction products in an infinitesimal time  $dt$  divided by that time. This concept is illustrated by the following problem.

*Prob. 1. — The Concept of Reaction-Rate.* — Sodium hydroxide and methyl acetate in dilute aqueous solution react with each other, as expressed by the equation:



Starting with a solution 0.01 weight-normal (wn.) in methyl acetate and sodium hydroxide and keeping the temperature constant at  $25^\circ$ , the concentrations of the methyl alcohol and sodium acetate (in milliequivalents per 1000 g. of water) after various times (in minutes) are found to be as follows:

Time . . . . .	0	2	5	10	20	40	8
Concentration . . . . .	0	1.91	3.70	5.41	7.02	8.25	10.00

- a.* Plot these concentrations as ordinates against the times as abscissas.
- b.* Determine from the plot the reaction-rate at the start, after 10 minutes, and after 30 minutes, stating the units in which the reaction-rate is expressed.
- c.* Suggest an analytical method by which the rate of this reaction could be followed experimentally.

**82. The Mass-Action Law of Reaction-Rate between Solutes.** — The effect of concentration on the rate of chemical changes between solutes is expressed by the following principle, known as the *mass-action law of reaction-rate*. The rate at any definite moment of a chemical reaction which takes place at a constant temperature between perfect solutes completely in one direction is proportional to the concentration, expressed either as weight-normality or normal concentration, of each of the reacting substances at that moment. That is, for the general case that any substances A, B, C, . . . react with one another:

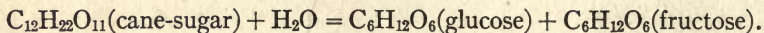
$$\frac{dc}{dt} = k C_A C_B C_C \dots$$

The proportionality-constant  $k$  which occurs in this equation is called the *specific reaction-rate*. It evidently represents the rate which the reaction would have, under the assumption of proportionality, if the weight-normality or the normal concentration of each of the reacting substances were unity.

This law is exact for perfect solutes; but, like other laws of perfect solutions, it holds true approximately up to moderate concentrations. The statement of the law here given is an incomplete one applicable only to reactions involving a single molecule of each of the reacting substances. A general statement of the law will be made after the mechanism of reactions has been considered.

**83. First-Order Reactions.** — The expression for the reaction-rate is simplest in the case of reactions in which only one substance undergoes a change in concentration. The rate in this case is expressed by a differential equation of the first degree; and such reactions are called *first-order reactions* or *unimolecular reactions*.

An example of a first-order reaction is the hydrolysis (splitting by water) of cane-sugar, which takes place in dilute aqueous solution in the presence of acid according to the equation:



Although two substances take part in this reaction, only one of them, the cane-sugar, need be considered; for the mass-action or concentration-effect of the water, being present in large excess, does not change appreciably during the course of the reaction. The acid acts catalytically, accelerating the reaction without being consumed by it. In formulating the reaction-rate equation and in evaluating the specific reaction-rate, it is usual to leave out of account the concentrations of substances which, like these, do not change with the progress of the reaction.

*Prob. 2. — Formulation of the Equations for First-Order Reactions. —*

*a.* Formulate the differential equation expressing the rate at which the hydrolysis of cane-sugar takes place, representing by  $c_0$  the concentration of the cane-sugar at the start, and by  $c$  the concentration of the glucose or fructose which has resulted at the time  $t$ . *b.* Integrate this equation between the time limits, 0 and  $t$ , and the corresponding limits of the concentration.

*Prob. 3. — Applications of the First-Order Equations. —* In a solution containing 0.3 mol of cane-sugar and 0.1 mol of HCl in 1000 g. of water, it is found (by measuring with a polarimeter the change in the optical rotatory power) that 32% of the sugar is hydrolyzed at 48° in 20 min-

utes. *a.* Calculate the specific reaction-rate and the actual rates at the beginning and at the expiration of 20 minutes. *b.* Calculate the percentage of sugar hydrolyzed after 40 minutes.

**84. Second-Order and Third-Order Reactions.** — Reactions whose rates are proportional to the concentrations of each of two substances or of each of three substances, are called *second-order* or *third-order reactions*, or *bimolecular* or *trimolecular reactions*. And in general, the *order of a reaction* is said to be equal to the degree of the differential equation expressing its rate.

*Formulation and Application of the Equations for Second-Order Reactions.* —

*Prob. 4.* — *a.* Formulate the differential equation expressing the rate in dilute aqueous solution of the reaction between methyl acetate and sodium hydroxide, in terms of the initial concentrations  $C_{A_0}$  and  $C_{B_0}$  of these two substances, and the concentration  $C$  of the reaction-products at the time  $t$ . *b.* Integrate this equation between the time limits 0 and  $t$  for the case that the initial concentrations of the two substances have the same value  $C_0$ . *c.* Integrate the equation (with the aid of a table of integrals, if preferred) also for the case that the initial concentrations  $C_{A_0}$  and  $C_{B_0}$  are different from each other.

*Prob. 5.* — When 0.01 mol of methyl acetate and 0.01 mol of NaOH are dissolved at 25° in 1000 g. of water, 11.8% of the ester is decomposed per minute at the start. *a.* Calculate the time required for one half of the ester in this mixture to be decomposed. *b.* Calculate the time required for this decomposition when 0.01 mol of methyl acetate and 0.02 mol of NaOH are dissolved in 1000 g. of water. *Ans.* *b.* 3.4 min.

The expressions for a reaction of a third order (between three substances A, B, and C) can be similarly derived.

For the case that all the substances involved have the same initial concentration  $C_0$  the integrated expressions for the three orders are:

$$\log \frac{C_0}{C_0 - C} = kt; \quad \frac{1}{C_0 - C} - \frac{1}{C_0} = kt; \quad \text{and} \quad \frac{1}{(C_0 - C)^2} - \frac{1}{C_0^2} = 2kt.$$

The following expressions for the fraction  $x$  of the reacting substances transformed can be derived from these integrated expressions for reactions of the first, second, and third orders:

$$\log \frac{1}{1-x} = kt; \quad \frac{x}{1-x} = ktC_0; \quad \text{and} \quad \frac{x(2-x)}{(1-x)^2} = 2ktC_0^2.$$

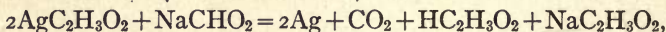
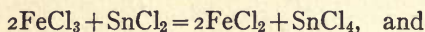
*Derivation and Application of the Expressions for the Fraction of the Reacting Substances Transformed.* —

*Prob. 6.* — Derive the expressions for the fraction transformed given in the preceding text.

*Prob. 7.* — At  $25^{\circ}$  the specific rate of the reaction between sodium hydroxide and methyl acetate is 1.8 times as great as that of the reaction between sodium hydroxide and ethyl acetate. Find the ratio of the times required for decomposing 90% of the two esters when equivalent quantities are present at the start.

*Prob. 8.* — Show from the above expressions how the time required for the transformation of any definite fraction of a definite quantity of the reacting substances would vary if the quantity of solvent in which they are dissolved were increased tenfold, *a*, in the case of the cane-sugar hydrolysis (Prob. 3); *b*, in the case of the decomposition of methyl acetate by sodium hydroxide (Prob. 5).

**85. The Mechanism of Reactions and the General Mass-Action Law of Reaction-rate.** — The rate of certain reactions, such as,



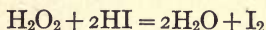
in which two molecules of one of the substances are involved, has been found to be proportional to the square (instead of to the first power) of the concentration of that substance. In other words, it is found that these reactions are of the third order, instead of the second order. This justifies the conclusion that the number of reacting molecules determines the law of the rate, and this conclusion is further substantiated by the fact that it harmonizes the mass-action law of reaction-rate with the mass-action law of chemical equilibrium (see Art. 98).

The provisional statement (Art. 82) of the law of reaction-rate should therefore be modified so as to state that the rate is proportional to the concentration of each of the reacting substances raised to a power equal to the number of its molecules which interact with the molecules of the other substances in the molecular process on which the occurrence of the reaction depends. Thus, in the case of a reaction  $aA + bB + cC \dots = eE + \dots$ , whose occurrence requires the interaction of *a* molecules of A, *b* molecules of B, *c* molecules of C, etc., the *mass-action law of reaction-rate* is expressed by the equation:

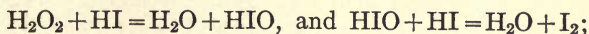
$$\frac{dc}{dt} = k (C_{A_0} - c)^a (C_{B_0} - c)^b (C_{C_0} - c)^c \dots$$

*Prob. 9.* — *Application of the Law of Reaction-Rate.* — Equal volumes of 0.2 *wn.* solutions of silver acetate ( $\text{AgC}_2\text{H}_3\text{O}_2$ ) and sodium formate ( $\text{NaCHO}_2$ ) are mixed at  $100^{\circ}$ ; and after definite intervals of time samples are removed, and the undecomposed silver acetate is titrated with potassium thiocyanate. Its weight-normality is found to be 0.067 after 2 minutes, 0.047 after 6 minutes, and 0.032 after 14 minutes. Show from these data that this reaction conforms more closely to the expression of the third order than to that of the second order.

It is found, however, that many reactions which apparently involve three or more molecules conform to the expression of the second order. This is probably to be explained by the consideration that the reaction expressed by the usual chemical equation takes place in stages, and that the stage which requires appreciable time is a reaction between two molecules. Thus the second-order reaction



may be considered to take place in the two stages,

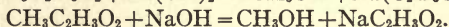
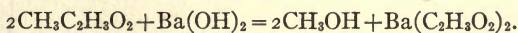


the first requiring a measurable time, and the second taking place almost instantaneously as soon as any HIO is formed by the first reaction. It is therefore necessary in the case of complex reactions to know their mechanism, that is, the molecular process by which they take place, in order to predict the law of their rate; and conversely, the law of the reaction-rate throws light on the mechanism of the reaction.

*The Mechanism of Reactions. —*

*Prob. 10.* — Suggest an explanation of the fact that the rate of the reaction  $\text{H}^+\text{BrO}_3^- + 6\text{H}^+\text{I}^- = \text{H}^+\text{Br}^- + 3\text{I}_2 + 3\text{H}_2\text{O}$  is proportional to the first power of the concentration of the  $\text{BrO}_3^-$  and of that of the  $\text{I}^-$ .

*Prob. 11.* — In aqueous solutions the measured rates of the chemical changes expressed by the following equations show that both of them are second-order reactions, and that they have not far from the same specific reaction-rates:



Suggest a mechanism that accounts for the fact that the first of these changes, like the second, is a reaction of the second order, and that the specific rates of the two reactions are not far from equal; and write an equation expressing the actual reaction whose rate determines the progress of the decomposition of the methyl acetate.

*Prob. 12.* — Assuming the correctness of the suggested mechanism of the methyl acetate decomposition, determine the quantity of free NaOH present (because of hydrolysis) in a 0.1 wn. NaCN solution at 25° from the fact that at 25° the initial rate of decomposition of methyl acetate is 9.0 times as great in a solution 0.01 wn. in NaOH as in a solution 0.1 wn. in NaCN.

**86. The Mass-Action Law of Reaction-Rate between Gaseous Substances.** — The general mass-action law (Art. 85) is applicable to the rate of reactions between gaseous substances in substantially the same form as to those between solutes. It is, however, usually

more convenient to express the concentrations in terms of mols per liter; but in that case it is necessary to refer the rate to a specified substance. Thus the rate of the reaction  $2A + B = 2E$  (for example,  $2NO + O_2 = 2NO_2$ ) at constant temperature may be expressed by any of the equations:

$$\frac{dc_E}{dt} = k c_A^2 c_B; \quad -\frac{dc_A}{dt} = k c_A^2 c_B; \quad -\frac{dc_B}{dt} = k' c_A^2 c_B, \quad \text{where } k' = \frac{1}{2}k.$$

For the case that the volume of the gas mixture remains constant, this equation expressed in terms of the molal concentrations of the reacting substances A and B at the start and the concentration of the product E at the time  $t$ , becomes:

$$\frac{dc_E}{dt} = k (c_{A0} - c_E)^2 (c_{B0} - \frac{1}{2}c_E).$$

It is important to note that many gas reactions are very sensitive to catalytic influences. In fact, it is not uncommon for gas reactions to take place to an appreciable extent only along the walls of the containing vessel. The rate of such catalytic or contact reactions is not determined by the mass-action law, which is applicable only to reactions that take place within the gas.

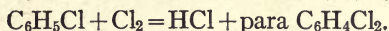
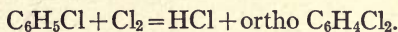
*Rate of the Reactions in the Arc Process of Nitrogen Fixation. —*

*Prob. 13.* — In the arc process of nitrogen-fixation air is brought in contact with an electric arc, the gas from the arc is rapidly cooled (by admixture with cold air and contact with the walls of the furnace), and under definite conditions the gas emerges from the furnace at  $1250^\circ$  and 1 atm. with a content of 2 mol-percent of nitric oxide (NO). Determine what percentage of this nitric oxide would be decomposed into nitrogen and oxygen if the gas was allowed to remain at  $1250^\circ$  for 10 minutes, from the facts that at this temperature the equilibrium conditions correspond to a substantially complete decomposition, and the specific reaction-rate in mols of NO destroyed per liter per minute is 50. *Ans.* 7.4.

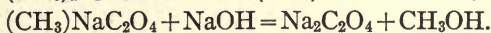
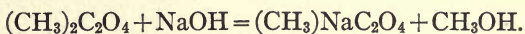
*Prob. 14.* — When the arc-process gas containing 2 mol-percent of nitric oxide is cooled at 1 atm. to  $20^\circ$  the reaction  $2NO + O_2 = 2NO_2$  takes place. From the facts that the specific reaction-rate in mols of  $NO_2$  produced per liter per second at  $20^\circ$  is 9400, and the equilibrium conditions correspond to substantially complete formation of  $NO_2$ , find the time that must be allowed to convert 90% of the NO into  $NO_2$ . (In integrating the differential equation regard as constant the volume of the mixture and the concentration of the oxygen.) *Ans.* 138 sec.

**87. Simultaneous Reactions.** — It often happens that two or more related reactions are taking place simultaneously. Some of the important types of such reactions are the following.

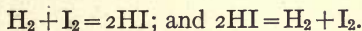
(1) A substance may be undergoing change in two different senses; thus, in the presence of iodine which acts as a catalyst, chlorobenzene and chlorine in carbon bisulfide solution undergo the two independent reactions represented by the equations:



(2) The products resulting from one reaction may undergo change by a second reaction; thus, when dimethyl oxalate and sodium hydroxide are brought together in aqueous solution, the following reactions take place consecutively:



(3) The products resulting from a reaction may tend to react with one another in the reverse direction. Thus hydrogen, iodine, and hydrogen iodide, in the gaseous state, undergo a (resultant) reaction in one or other of the two directions expressed by the following equations, depending on the concentrations of the respective substances:



In the case of such reactions taking place simultaneously, the rate of each is determined by its own specific reaction-rate and by the concentrations of the substances involved in it, just as if the other reaction were not taking place. In accordance with this *law of independence of reaction-rates* the differential equations expressing the rates can be formulated.

*Formulation of the Rates of Simultaneous Reactions. —*

\**Prob. 15.* — Calculate the specific reaction-rates  $k_1$  and  $k_2$  of the two reactions considered in case (1) above, supposing that at some definite temperature and with a definite iodine concentration it were found that in a  $\text{CS}_2$  solution initially 0.5 f. in  $\text{C}_6\text{H}_5\text{Cl}$  and 0.5 f. in  $\text{Cl}_2$  15% of the  $\text{C}_6\text{H}_5\text{Cl}$  is converted into ortho  $\text{C}_6\text{H}_4\text{Cl}_2$  and 25% into para  $\text{C}_6\text{H}_4\text{Cl}_2$  in 30 minutes. *Ans.*  $k_1 = 0.0167$ ;  $k_2 = 0.0278$ .

\**Prob. 16.* — Noting that in case (2) the intermediate compound  $\text{CH}_3\text{NaC}_2\text{O}_4$  is constantly produced by the first reaction and destroyed by the second reaction, formulate a differential equation for the resultant rate  $dc_A/dt$  at which this compound is formed, in terms of the initial molalities  $c_0$  and  $2c_0$  of the  $(\text{CH}_3)_2\text{C}_2\text{O}_4$  and  $\text{NaOH}$ , respectively and of the molalities  $c_A$  and  $c_B$  of  $(\text{CH}_3)\text{NaC}_2\text{O}_4$  and  $\text{Na}_2\text{C}_2\text{O}_4$ , respectively, that have resulted at any time  $t$ .

*Prob. 17.* — *a.* Formulate an expression for the (resultant) rate at which HI is produced in a gaseous mixture by the equation given in case (3) in terms of the molal concentrations  $C_H$ ,  $C_I$ ,  $C_{HI}$ , of the substances at any time  $t$ . *b.* Noting that there will be equilibrium when the rate of formation of HI by the direct reaction becomes equal to the rate of its decomposition by the reverse reaction, derive an expression for the equilibrium conditions of this reaction.

In general, for any reaction represented by the chemical equation:



the expression derived (in the way illustrated by Prob. 17) from the general law of reaction-rate (Art. 85) for the equilibrium conditions at any definite temperature is

$$\frac{c_E^e c_F^f \dots}{c_A^a c_B^b \dots} = \frac{k_1}{k_2} = K, \text{ a constant.}$$

The constancy of this concentration product is the expression of the mass-action law of chemical equilibrium, as will be shown in Art. 98.

This result is of importance not only as a derivation of that law, but also because it shows that the equilibrium-constant  $K$  is the ratio  $k_1/k_2$  of the specific rates of the two opposing reactions. In other words, equilibrium does not signify a condition in which no change is taking place, but one in which the two opposing reactions are taking place at equal rates.

## II. THE EFFECT OF CONCENTRATION AND SURFACE ON REACTIONS BETWEEN SOLUTIONS AND SOLID SUBSTANCES

### 88. Rate of Reaction between Solutes and Solid Substances. —

When a solute is reacting with a solid substance the quantity of the solid acted upon per unit of time is proportional to the surface of the solid and to the concentration of the solute that reacts with it. Thus, when a dilute solution of acetic acid in contact with a compact mass of magnesium oxide is uniformly stirred, the quantity of the solid dissolved is proportional to the surface of the mass and to the concentration of the acetic acid.

In reactions with solid substances, it is to be borne in mind that, owing to corrosion, the effective surface is constantly changing, and that the concentration of the solution in contact with the solid is the same as that of the whole solution only when there is adequate stirring.

89. Solid Substances Dissolving in their Own Solutions. — When a solid substance is dissolving at a definite temperature in its own partially saturated solution, the rate  $dc/dt$  at which the concentration of the solution increases is proportional to the difference between the saturation-concentration  $s$  and the actual concentration  $c$ , and to the area  $a$  of the surface of the solid, and it is inversely proportional to the volume  $v$  of the solution; that is,

$$\frac{dc}{dt} = k \frac{a}{v} (s - c).$$

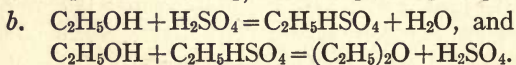
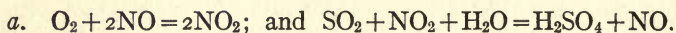
*Prob. 18. — Rate of Saturation of a Solution. —* A definite quantity of a solid substance is shaken with a definite volume of water at  $25^{\circ}$ .  
*a.* Calculate the time of shaking required to produce 60, 90, and 98 percent saturation, assuming that the solution becomes 30% saturated in one minute, and that the surface of the solid remains constant.  
*b.* With the aid of these values make a diagram showing how the percentage saturation increases with the time of shaking. *c.* Find from the diagram the time required to produce 95% saturation, and the time required to increase the saturation from 95% to 98%.

## III. THE EFFECT OF CATALYSTS

**90. Catalysis.** — A reaction is often greatly accelerated by the presence of a substance which is not itself consumed by the reaction. This phenomenon is called *catalysis*, and the substance producing it is called the *catalyst*.

Although few general principles relating to catalysis have been established, its great practical importance makes it desirable to consider the common types of catalysts and the ways in which they act.

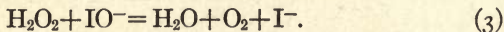
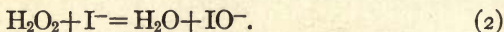
**91. Carriers.** — Carriers constitute one of the most common and best understood types of catalysts. The mechanism of their action is as follows: The catalyst produces with one of the substances an intermediate compound which reacts with the second substance in such a way as to regenerate the catalyst, the reaction of the second substance with the intermediate compound taking place more rapidly than that with the first substance. In this way a reaction which does not take place directly at an appreciable rate may be made to take place in stages at a rapid rate. The chamber process of making sulfuric acid and the technical method of making ether are familiar examples of this type, the fundamental reactions being:



The mechanism of carrier catalysis is well illustrated by the decomposition of hydrogen peroxide, which in aqueous solution takes place in accordance with the equation:

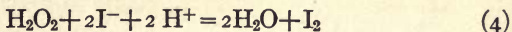


This decomposition is very slow when the hydrogen peroxide is present alone, but becomes rapid in the presence of a moderate concentration of iodide-ion. The principles (considered in Probs. 19 and 20) determining the rate of the reaction seem to show that this catalytic effect is due to the occurrence of the reaction in the two stages represented by the equations:

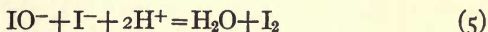


In the presence of a considerable concentration of hydrogen-ion, as well as of iodide-ion, the hydrogen peroxide does not decompose to an important extent into water and oxygen in accordance with equation (1),

but it yields water and iodine in accordance with the following equation:



The rate of this reaction is found, however, to be proportional to the iodide-ion concentration (not to its square) and to be dependent in only a secondary degree on the concentration of the hydrogen-ion. This can be accounted for by considering that reaction (4) takes place in two stages, namely, that represented by equation (2) above, and that represented by the following equation; this last reaction occurring almost instantaneously and completely when the hydrogen-ion concentration is large:



*The Mechanism of Carrier Catalysis. —*

*Prob. 19.* — State and formulate the principles that would express the rate of the decomposition of hydrogen peroxide in neutral solution in the presence of iodide-ion, assuming that it takes place, *a*, directly according to reaction (1); *b*, according to reactions (2) and (3), the latter taking place instantaneously; *c*, according to reactions (2) and (3), the  $\text{IO}^-$  produced by (2) soon attaining such a concentration that reaction (3) thereafter takes place at the same rate as reaction (2). (Case *c* seems to represent what actually occurs.)

*Prob. 20.* — *a.* Show by reference to the equilibrium conditions of reaction (5) why reaction (3), and therefore reaction (1), does not take place to any important extent in the presence of a considerable concentration of hydrogen-ion; also why reaction (5), and therefore reaction (4), does not take place to an important extent in a nearly neutral solution. *b.* Show what relative quantities of hydrogen peroxide would, if these explanations are correct, be decomposed per minute in a solution 0.1 formal in  $\text{H}_2\text{O}_2$  and 0.1 formal in KI in the two cases that the solution is neutral and that it is moderately acid with HCl.

**92. Contact Agents.** — Reactions between gases or solutes are often greatly accelerated by placing the reacting mixture in contact with a suitable solid substance which offers a large surface. The heavier metals are especially likely to be effective; but many other substances have specific effects on definite reactions. The platinum contact-process of making sulfur trioxide from sulfur dioxide and oxygen and the Deacon process of making chlorine by passing hydrogen chloride and oxygen over a porous mass impregnated with copper chloride are examples of contact catalysis. As already stated in Art. 86, gas reactions are often catalyzed by solid surfaces to such an extent that

the chemical change takes place appreciably only in the surface layer on the walls of the containing vessel or on other solid material in contact with the gas, and the rate of such reactions does not conform to the mass action law.

The mechanism of contact actions is little understood. In most cases, the contact action is probably due to an *adsorption* of the reacting substances (that is, to a deposition of them on the surface of the solid) and to the fact that in the surface-layer the reaction-rate is greatly increased. Thus, finely divided platinum placed in contact with illuminating gas and air adsorbs the gases, and these then react so rapidly as to cause the gas to take fire.

**93. Hydrogen-Ion and Hydroxide-Ion as Catalysts.** — In aqueous solutions many reactions are accelerated by hydrogen-ion. This is probably true of all reactions in which water is directly involved, such as the hydrolysis of cane-sugar or of esters. It is also true of certain reactions of oxidation and reduction.

The specific rate of such hydrolytic reactions in dilute solutions is found to be proportional to the concentration of the hydrogen-ion; for example, the specific reaction-rate of the cane-sugar hydrolysis at  $48^{\circ}$  has been found to be 9.95 times as great in 0.01 normal as it is in 0.001 normal HCl solution. At higher hydrogen-ion concentrations or in the presence of neutral salts considerable deviations from proportionality exist; thus, the rate of the cane-sugar hydrolysis is 10.5 times as great in 0.1 normal as in 0.01 normal HCl solution.

This principle can be employed (as shown by Prob. 22) for determining the hydrogen-ion concentration in solutions; for no other ion (except hydroxide-ion in certain cases) exerts a catalytic effect on hydrolytic reactions.

Reactions in which water takes part are often accelerated also by hydroxide-ion; thus, milk-sugar,  $C_{12}H_{22}O_{11}$ , dissolved in water becomes hydrated (with formation of  $C_{12}H_{22}O_{11} \cdot H_2O$ ) at a rate which is greatly increased by hydroxide-ion.

*Prob. 21. — Possible Explanation of the Catalytic Effect of Hydrogen-Ion.* — Show by writing chemical equations how the catalytic effect of hydrogen-ion on hydrolytic reactions may be interpreted as a carrier action, assuming that the hydrogen-ion is hydrated.

*Prob. 22. — Determination of Hydrogen-Ion Concentration through its Catalytic Effect.* — Diazoacetic ester decomposes in aqueous solution according to the equation  $CHN_2 \cdot CO_2C_2H_5 + H_2O = CH_2OH \cdot CO_2C_2H_5 + N_2$ , and the reaction is catalyzed by hydrogen-ion. At  $25^{\circ}$  in a solution 0.1

formal in acetic acid, whose ionization is 1.34%, it is found by measuring the nitrogen evolved that 37.5% of the ester is decomposed in 10 minutes. Assuming that it takes 67 minutes to decompose the same percentage of the ester in a solution 0.1 formal in sodium hydrogen tartrate, calculate the molality of hydrogen-ion in that solution.

**94. Enzymes.** — Certain complex organic substances, called *enzymes*, which are produced by animal and plant organisms, have an extraordinary power of catalyzing certain organic reactions. The effect is highly specific, a particular enzyme being required for a particular reaction. Thus invertase, an enzyme produced by yeast, causes the conversion of cane-sugar into glucose and fructose; and xymase, another yeast enzyme, causes the conversion of glucose, but not of the analogous compound fructose, into ethyl alcohol and carbon dioxide.

**95. Water as a Catalyst.** — The presence of water in at least minute quantity is essential to the occurrence of almost all reactions. This is shown by experiments upon some of the most energetic chemical changes, which are found not to take place when the separate substances are very thoroughly dried before they are brought together. Thus, this is true of the combination of sodium with chlorine, the union of ammonia and hydrogen chloride gases, the combustion of carbon monoxide with oxygen, and the union of lime and sulfur trioxide.

## IV. THE EFFECT OF TEMPERATURE

**96 Principles Relating to the Effect of Temperature.** — Measurements of the change with the temperature of the rates of reactions taking place between solutes or between gases have shown that as a rule equal small increments of temperature cause an approximately equal multiplication of the specific rate of any definite reaction. Thus, if the specific rate of a reaction is increased 2.5 fold by raising the temperature from 0 to 10°, it will again be increased approximately 2.5 fold by raising the temperature from 10 to 20°. This principle and the order of magnitude of the deviations from it are illustrated by the following data for the third-order reaction between ferrous chloride, potassium chlorate, and hydrochloric acid. The values  $k_1/k_2$  are the ratios of the specific reaction-rates at 10° intervals.

	10 to 0°	20 to 10°	30 to 20°	40 to 30°	50 to 40°
$k_1/k_2$	2.8	2.7	2.5	2.4	2.2

A more general and more exact expression of the effect of temperature is that given by the following equations, in which  $A$  is a constant for any definite reaction:

$$d \log k = A \frac{dT}{T^2}; \text{ or } \log \frac{k_2}{k_1} = A \frac{T_2 - T_1}{T_1 T_2}.$$

It is evident that, so long as the variation of  $T_1 T_2$  is not large, the approximate principle is a consequence of this more general law.

*Prob. 23. — The Effect of Temperature.* — *a.* In a solution 0.01 molar in sodium hydroxide and 0.01 molar in ethyl acetate, 39% of the ethyl acetate is decomposed in 10 minutes at 25°, and 55% at 35°. Determine by the approximate principle how long it would take to decompose 55% at 15°. *b.* Calculate by the logarithmic equation how long it would take to decompose 50% of the ethyl acetate at 20°.

It has also been found that in the case of different reactions equal small increments of temperature cause not far from the same multiplication of their specific rates. Thus, a 10° rise of temperature multiplies the specific rate of the reaction between sodium hydroxide and ethyl acetate 1.9 fold, of that between cane-sugar and water in the presence of acid 3.6 fold, and of that between ferrous sulfate, potassium chlorate, and sulfuric acid 2.4 fold.

*Prob. 24. — Uniform Effect of Temperature on Different Reactions.* — At 100° a certain reaction takes place to an extent of 25% in one hour. Estimate roughly how long it would take for the reaction to proceed to the same extent at 20°.

## CHAPTER VII

### THE EQUILIBRIUM OF CHEMICAL CHANGES AT CONSTANT TEMPERATURE

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#### I. THE LAW OF MASS-ACTION

**97. The Equilibrium of Chemical Reactions.** — When two or more chemical substances capable of reacting with one another are brought together, it is always true after a sufficiently long time (which may vary from a fraction of a second to thousands of years) that the chemical reaction which has been taking place between them practically ceases — in other words, that a condition is reached where no further change takes place. The reaction is then said to be in *equilibrium*.

Many reactions (for example, the reaction  $\text{NH}_4\text{OH} + \text{HBO}_2 = \text{NH}_4\text{BO}_2 + \text{H}_2\text{O}$  in aqueous solution) take place so incompletely that at equilibrium the substances on both sides of the equation are present in measurable proportions. But with many other reactions the equilibrium-conditions are such that the change seems to take place completely when the substances on one side of the chemical equation expressing it are brought together, and not to take place at all when the substances on the other side are brought together; thus, this is true of the reaction  $\text{NaOH} + \text{HCl} = \text{NaCl} + \text{H}_2\text{O}$  in aqueous solution. In all such cases, however, the gaseous or dissolved substances on both sides of the equation are really present at some concentration, though this may be so small in the case of some of the substances that it cannot be directly measured.

Reactions (like that in a mixture of hydrogen and oxygen at  $25^\circ$ ) which are taking place so slowly that no appreciable change can be detected within a reasonable time are not to be confounded with those which are in a state of equilibrium. Whether equilibrium-conditions have been attained can be determined by causing the reaction to take place in the two opposite directions and comparing the concentrations of the substances in the two cases after equilibrium seems to have been reached.

The equilibrium conditions of chemical reactions vary with the temperature, as considered in Chapter XII. In this chapter the principles will be discussed which determine equilibrium when the temperature has any constant value.

**98. The Mass-Action Law of Chemical Equilibrium.** — The effect of concentration in determining chemical equilibrium is expressed by one of the most fundamental laws of chemistry. This law, which is commonly known as the *mass-action law*, states that, whatever be the initial concentrations of the gaseous or dissolved substances A, B, . . . E, F, . . . involved in any definite chemical reaction, such as may be represented in general by the equation,  $aA + bB \dots = eE + fF \dots$ , the reaction always takes place in such a direction and to such an extent that, when equilibrium is reached at any definite temperature, the conditions are satisfied which are expressed by the equation:

$$\frac{c_E^e c_F^f \dots}{c_A^a c_B^b \dots} = K, \text{ a constant.}$$

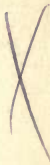
In this expression  $c_E, c_F, \dots c_A, c_B, \dots$  denote either the molal concentrations or molalities of the substances E, F, . . . A, B, . . . in the equilibrium mixture, and  $e, f, \dots a, b, \dots$  denote the number of mols of them that are involved in the reaction expressed by the chemical equation. A simpler notation commonly employed is to represent the molalities of solutes at equilibrium by their formulas enclosed within parentheses; thus, by writing (E) in place of  $c_E$ , etc.

The quantity  $K$ , which is a constant characteristic of the reaction, is called its *equilibrium-constant*. Its value is, of course, constant with respect to variations of the initial and equilibrium concentrations, but it varies with the temperature. In evaluating it, molal concentrations will be used in the case of gases, and molalities (defined as in Art. 35) in the case of solutions. It is customary to place in the numerator the concentrations of the substances occurring on the right-hand side of the chemical equation written in some specified way. In which direction the chemical equation is written is, of course, arbitrary in the case of reactions at equilibrium. With many types of reactions, however, it is more natural to write the equation in one of the two directions; and in such cases the usage in evaluating the equilibrium-constant has become fairly definite. This usage will be illustrated by the examples given in the following articles.

The mass-action law of equilibrium is a consequence of the mass-action law of reaction-rate, as shown in Art. 87. It can also be derived with the aid of the laws of thermodynamics from the physical laws of perfect gases and of perfect solutions, as shown in Arts. 140 and 141. It has also been established by experimental investigations on the equilibrium of a large number of different reactions.

The mass-action law is exact, as is shown by its derivation, only in the case of reactions between perfect gases or perfect solutes; but it holds true approximately when applied to gases at moderate pressures, to unionized solutes at moderate concentrations, and to ions at small concentrations. The deviations from it in such cases may be expected to be of the same order of magnitude as those from the physical laws of perfect gases or perfect solutions.

Although the mass-action law of chemical equilibrium has been derived from the mass-action law of reaction-rate, an important difference between the two laws is to be noted. Namely, it can be shown that, although the expression for the rate of a reaction depends on its mechanism, the same expression is obtained for its equilibrium, whatever be the process by which that equilibrium is considered to be attained. In using the equilibrium expression it is necessary to know only the concentrations of the substances actually occurring in that expression.



## II. THE MASS-ACTION LAW FOR REACTIONS BETWEEN GASES

**99. The Mass-Action Law in Terms of Partial Pressures.** — In applications of the mass-action law to gases, it is usual to substitute for the concentrations of the substances in the equilibrium-mixture their partial pressures. This is admissible since at any definite temperature the two quantities are proportional to one another in the case of perfect gases, in virtue of the relation  $p = cRT$ .

The general mass-action expression in terms of partial pressures evidently is

$$\frac{p^e p_r^f \dots}{p_A^a p_B^b \dots} = K_p,$$

where  $K_p$  is a constant, called the *equilibrium-constant in terms of pressure*, which has in general a different numerical value from the constant  $K$  occurring in the corresponding concentration-expression. In evaluating it the partial pressures are commonly expressed in atmospheres.

*Prob. 1.* — *Relation between the Equilibrium Expressions in Terms of Concentrations and Pressures.* — Derive the general mass-action expression in terms of pressure from that in terms of concentration, and show the relation between the two equilibrium-constants.

**100. Gaseous Dissociation.** — A chemical change which consists in the splitting of a substance with complex molecules into one or more substances with simpler molecules is called dissociation. Thus, the reactions  $I_2 = 2I$ ,  $NH_4Cl = NH_3 + HCl$ , and  $2CO_2 = 2CO + O_2$ , are examples of dissociation. The fractional extent to which the dissociating substance has been decomposed is called its degree of dissociation, or simply its *dissociation* ( $\gamma$ ). The equilibrium-constant of such a reaction is commonly called the *dissociation-constant* of the dissociating substance.

It is characteristic of such reactions that the number of molecules increases when the dissociation increases. Since the pressure-volume product of gases increases correspondingly, the degree of dissociation can always be determined by measuring the volume or density of the gas at a known temperature and pressure, and comparing it with that calculated for the undissociated or completely dissociated substance, as is illustrated by Probs. 10 and 11 of Art. 12, and by Prob. 3 below.

Another common method of determining the composition of the equilibrium mixture is to cool it suddenly to a lower temperature at

which the reaction-rate is so small that the original equilibrium is not displaced, and then to analyze the mixture. This method presupposes that there is no change in the composition during the short period of cooling. This condition may be practically realized in cases where the rate at which the equilibrium is established is comparatively slow even at the higher temperature, or in cases where the reaction takes place only in contact with a catalyst. In the latter cases the equilibrium-mixture can be separated from the catalyst, and subsequently cooled without the danger of any change taking place.

*Applications of the Mass-Action Law to Gaseous Dissociation. —*

*Prob. 2. — a.* Formulate the mass-action expression for the dissociation of sulfur trioxide into sulfur dioxide and oxygen. *b.* At  $630^{\circ}$  and 1 atm. the sulfur trioxide is just one third dissociated. Calculate the dissociation-constant of sulfur trioxide.

*Prob. 3. —* Show how the dissociation ( $\gamma$ ) of sulfur trioxide could be calculated from measurements of the density ( $d$ ) of the equilibrium mixture at the temperature ( $T$ ) and pressure ( $p$ ).

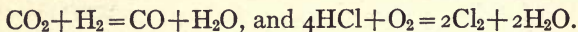
*Prob. 4. —* A mixture consisting of 1 mol of  $\text{SO}_2$  and 1 mol of  $\text{O}_2$  is passed at  $630^{\circ}$  and 1 atm. through a tube containing finely divided platinum so slowly that equilibrium is attained, and the issuing gas is cooled and analyzed by absorbing the sulfur dioxide and trioxide by potassium hydroxide and measuring the residual oxygen gas. At  $0^{\circ}$  and 1 atm. the volume of this residual gas was found to be 13,780 ccm., corresponding to 0.615 mol. *a.* Calculate the dissociation-constant of sulfur trioxide. *b.* Calculate the ratio of the mols of sulfur trioxide to the mols of sulfur dioxide in an equilibrium mixture at  $630^{\circ}$  in which the partial pressure of oxygen is 0.25 atm.

*Prob. 5. —* At a certain temperature a definite quantity of phosphorus pentachloride gas has at 1 atm. a volume of 1 liter, and under these conditions it is about 50% dissociated into  $\text{PCl}_3$  and  $\text{Cl}_2$ . Show by reference to the mass-action expression whether the dissociation will be increased or decreased: *a.* when the pressure on the gas is reduced till the volume becomes 2 l.; *b.* when nitrogen is mixed with the gas till the volume becomes 2 l., the pressure being still 1 atm.; *c.* when nitrogen is mixed with the gas till the pressure becomes 2 atm., the volume being still 1 l.; *d.* when chlorine is mixed with the gas till the pressure becomes 2 atm., the volume being still 1 l.; *e.* when chlorine is mixed with the gas till the volume becomes 2 l., the pressure being still 1 atm. — In answering these questions consider whether the first effect of the change in conditions (assuming that no reaction takes place) is to increase or decrease the value of the ratio  $p_{\text{Cl}_2} p_{\text{PCl}_3} / p_{\text{PCl}_5}$ , and in which direction the reaction must take place in order to restore the equilibrium-value of this ratio.

*Prob. 6. — a.* Derive for the dissociation of water-vapor into hydrogen and oxygen a mass-action expression which will show how the dissocia-

tion  $\gamma$  varies with the total pressure  $p$ . *b.* At  $2000^\circ$  the dissociation is 2.0% when the total pressure is 1 atm. Calculate the dissociation when the total pressure is 0.33 atm. (as it is approximately in the gaseous mixture produced by burning hydrogen with the minimum amount of air). Solve the equation approximately, neglecting the (small) value of the dissociation where this is justifiable. *Ans. b, 2.9%.*

**101. Metathetical Gas Reactions.** — Examples of metathetical gas reactions whose equilibrium has been investigated are:



An important principle in regard to them, illustrated by Prob. 8 below, is that the equilibrium-constant of any metathetical gas reaction can be calculated from the dissociation-constants of the compounds involved in it.

Another important principle relates to the effect of pressure. It states that increase of pressure causes the equilibrium of any gaseous reaction to be displaced in that direction in which the number of molecules, and therefore the volume of the gas, decreases. This principle has already been illustrated by the fact that dissociation is decreased by increase of pressure. It is demonstrated in Prob. 9.

*Prob. 7. — Combustion of "Water-Gas" with Insufficient Oxygen.* — The equilibrium-constant of the reaction  $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$  at  $1120^\circ$  is 2.0. Calculate the ratio of the mols of  $\text{CO}_2$  to the mols of  $\text{H}_2\text{O}$  that are formed when a "water-gas" consisting of 1 mol of CO and 1 mol of  $\text{H}_2$  is burnt at  $1120^\circ$  with  $\frac{1}{2}$  mol of  $\text{O}_2$ . Assume that equilibrium is attained and that the quantity of the oxygen which remains uncombined is negligible.

*Prob. 8. — Metathetical Equilibrium-Constants in Relation to Dissociation-Constants.* — The equilibrium-constant of the reaction  $2\text{CO}_2 = 2\text{CO} + \text{O}_2$  at  $1120^\circ$  is  $1.4 \times 10^{-12}$ . *a.* Calculate the partial pressure of the oxygen in the equilibrium mixture of Prob. 7. *b.* Calculate the dissociation-constant of water-vapor at  $1120^\circ$ . *c.* Show what relation exists between the dissociation-constants  $K_w$  and  $K_{\text{CO}_2}$  of water-vapor and of carbon dioxide and the equilibrium-constant  $K$  of the reaction  $\text{CO}_2 + \text{H}_2 = \text{CO} + \text{H}_2\text{O}$ . *Ans. b,  $3.5 \times 10^{-13}$ .*

*Prob. 9. — Effect of Pressure on Gaseous Equilibrium.* — Prove that the equilibrium of any chemical reaction,  $aA + bB = eE + fF$ , must be displaced in the direction in which the number of molecules decreases when the total pressure  $p$  of the equilibrium mixture (in which the substances are present at mol-fractions  $x_A$ ,  $x_B$ ,  $x_E$ , and  $x_F$ ) is increased.

*Prob. 10. — Production of Hydrogen from "Water-Gas."* — A quantity of "water-gas" consisting of 1 mol of CO and 1 mol of  $\text{H}_2$  is mixed with 5 mols of steam, and this mixture is passed slowly at 1 atm. and  $500^\circ$  over a suitable catalyst, whereby the reaction  $\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$

takes place. The gases are then cooled in order to condense the steam. The equilibrium-constant of the reaction at  $500^{\circ}$  is 5.5. *a.* Calculate the smallest mol-fraction of CO in the resulting gas mixture attainable by this process. *b.* Show whether this minimum percentage of CO could be diminished by passing the gas mixture over the catalyst at 5 atm. and  $500^{\circ}$ . *c.* Show whether it could be diminished by passing it over the catalyst at 1 atm. and  $400^{\circ}$ , noting the values of the equilibrium-constant already given at  $1120^{\circ}$  and  $500^{\circ}$ . *d.* State the effect of the lower temperature on the time required for reducing the percentage of CO to any definite value. *e.* In practice the above process may yield a mixture containing 4 mol-percent of CO, 65 mol-percent of  $H_2$ , and 31 mol-percent of  $CO_2$ . To free this mixture from  $CO_2$ , it is passed at 30 atm. up a tower through which water at  $17^{\circ}$  is trickling. Calculate the minimum volume of water theoretically required to remove 99% of the  $CO_2$  from 100 mols of the gas mixture. Assume Henry's law to hold true, and take the solubility of  $CO_2$  in water at  $17^{\circ}$  and 1 atm. as 0.0425 molal. *f.* Calculate the percentage of the hydrogen that is lost by dissolving in the water, from the fact that the solubility of hydrogen gas in water at  $17^{\circ}$  and 1 atm. is 0.00084 molal. *Ans.* *e.*, 77.7 liters.

## III. THE MASS-ACTION LAW FOR REACTIONS BETWEEN SOLUTES

## 102. Ionization of Slightly Ionized Univalent Acids and Bases. —

The mass-action law has been found to be applicable to the ionization of the slightly ionized monobasic acids and monacidic bases. This is illustrated by the following values at 18° of the ionization, taken equal to the conductance-viscosity-ratio, and of the *ionization-constant*  $K$  for ammonium hydroxide, that is, the equilibrium-constant of the reaction  $\text{NH}_4\text{OH} = \text{NH}_4^+ + \text{OH}^-$ .

## IONIZATION OF AMMONIUM HYDROXIDE AT 18°

Formality	0.500	0.300	0.100	0.010	0.001
Ionization	0.0056	0.0074	0.0130	0.0405	0.123
$K \times 10^6$	15.8	16.6	17.1	17.1	17.1

The ionization-constant varies greatly with the composition and structure of the acid or base, as will be seen from the following values.

## IONIZATION-CONSTANTS OF ACIDS AND BASES AT 25°

Acid	$10^6 K$	Acid	$10^6 K$	Acid	Values of $10^6 K$		
HCN	0.0005	HCO <sub>2</sub> H	210	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H	60	60	60
HBO <sub>2</sub>	0.0017	CH <sub>3</sub> CO <sub>2</sub> H	18		Ortho	Meta	Para
HClO	0.044	C <sub>2</sub> H <sub>5</sub> CO <sub>2</sub> H	13	C <sub>6</sub> H <sub>4</sub> OHCO <sub>2</sub> H	1020	87	29
HNO <sub>2</sub>	400.	<i>n</i> -C <sub>3</sub> H <sub>7</sub> CO <sub>2</sub> H	15	C <sub>6</sub> H <sub>4</sub> ClCO <sub>2</sub> H	1320	155	93
HF	790.	CH <sub>2</sub> ClCO <sub>2</sub> H	1550	C <sub>6</sub> H <sub>4</sub> NO <sub>2</sub> CO <sub>2</sub> H	6160	345	396
<hr/>							
		Base	$10^6 K$				
		NH <sub>4</sub> OH	18.				
		CH <sub>3</sub> NH <sub>2</sub> OH	500.				
		C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> OH	0.0004				

*Prob. 11. — Derivation of Ionization-Constants from Conductance Data. — a.* Calculate the ionization-constant of acetic acid at 18° at the concentrations 0.01, 0.1, and 1.0 formal, from the conductance values given in Art. 74. *b.* Calculate the ionization-constants at 0.1 and 1.0 formal, taking into account the fact that the viscosity of the 1 formal solution is 1.113 times as great as that of pure water. *c.* Calculate the ionization of the acid and its equivalent conductance in 0.001 formal solution.

*Prob. 12. — Effect of the Presence of a Substance with a Common Ion. — a.* Show that the hydrogen-ion concentration in an acetic acid solution is decreased by the addition of sodium acetate approximately in the proportion in which the concentration of the acetate-ion is increased. *b.* Calculate the ionization of acetic acid in a solution 0.1 formal both in acetic acid and in sodium acetate at 18°, regarding the sodium acetate as completely ionized. — In this and other mass-action problems make any simplifications that will not produce in the result an error greater than 1%.

✓ **103. Ionization of Largely Ionized Substances.** — As was stated in Art. 79, the conductance-ratio of salts and largely ionized acids and bases does not change with the concentration even approximately as the mass-action would require if that ratio were equal to the ionization. Now that the mass-action law has been formulated, the degree of the divergence can be shown quantitatively. The following table contains the values (designated  $\gamma$  observed) of the conductance-viscosity ratio for potassium chloride, the ionization-constants ( $K$ ) calculated from them by the mass-action expression  $(\gamma c)^2/(1-\gamma)c$ , and the ionization-values ( $\gamma$  calculated) computed conversely from the value of the ionization-constant at 0.1 formal.

THE CONDUCTANCE-RATIO IN RELATION TO THE MASS-ACTION LAW

Formality . . .	0.001	0.01	0.05	0.10	0.20	0.50	1.00
$\gamma$ observed . . .	0.982	0.94	0.89	0.86	0.83	0.78	0.74
$\gamma$ calculated . . .	0.998	0.98	0.92	0.86	0.78	0.63	0.51
Ionization-constant	0.053	0.15	0.36	0.53	0.81	1.38	2.10

. This striking discordance with the mass-action law and certain other anomalies, some of which were discussed in Art. 79, have led, as already stated, to the conclusion that the conductance-ratio or the conductance-viscosity-ratio is not even an approximate measure of the mass-action of the ions or unionized molecules of largely ionized substances. It will be shown in Art. 113 that there is a general method, differing in principle from the conductance method, by which there can be derived the mass-action of substances (that is, their effect in determining equilibria) in cases where the mass-action is not proportional to the concentration as the mass-action law requires. The data needed in order to calculate by this method the mass-action of such imperfect solutes are, however, very incomplete; and the following simple hypotheses lead to results which usually do not differ by more than a few percent from the results derived with the aid of the exact principle, in the case of solutes not more concentrated than 1 formal. These hypotheses are that largely ionized substances are completely ionized and that their ions act as perfect solutes. These hypotheses are therefore employed throughout this chapter in all the applications of the mass-action law to the different types of equilibrium between dissolved substances, and they are to be used in solving all the problems. In Art. 113 at the end of this chapter a method suitable for the exact treatment of ordinary solutes at large concentration, and of ions at small concentrations, will be described.

**104. The Ionization of Water.** — The dissociation of water into  $H^+$  and  $OH^-$  ions is extremely small, as is shown by the very small conductance of the purest water that has been prepared. This ionization is, nevertheless, of great significance from an equilibrium viewpoint, since water is involved in many ionic reactions, for example, in the hydrolysis of salts considered in Art. 105.

The complete expression for the equilibrium-constant of the reaction  $H_2O = H^+ + OH^-$  would contain a term representing the mass-action of the chemical substance  $H_2O$ . In the case of a substance so concentrated, it is not justifiable to represent its mass-action by its concentration, since the mass-action law is applicable only to substances at small concentrations. It will, however, be shown in Art. 113 that the mass-action of a substance in a solution of any concentration is proportional to its vapor-pressure in that solution; hence the equilibrium-constant for the ionization of water is accurately expressed by the equation  $K = (H^+)(OH^-)/p_{H_2O}$ . Now, since the vapor-pressure of water in a 1 molal solution of any solute is according to Raoult's law only 1.8 percent less than that of pure water, the mass-action of the water is nearly constant in aqueous solutions of moderate concentration; and the equilibrium-constant of the reaction, commonly called the *ionization-constant*  $K_w$  of water, may be written in the simple form:  $K_w = (H^+)(OH^-)$ .

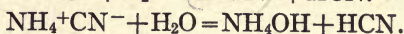
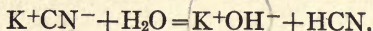
The ionization-constant of water has been determined by a number of different methods including that based on the conductance of carefully purified water, illustrated by Prob. 34 of Art. 77. Its value has been found to be  $0.11 \times 10^{-14}$  at  $0^\circ$ ;  $1.00 \times 10^{-14}$  at  $25^\circ$ ; and  $48 \times 10^{-14}$  at  $100^\circ$ .

From the value of this ionization-constant there can be calculated the concentration of hydrogen-ion in any dilute aqueous solution of known hydroxide-ion concentration, and conversely.

*Prob. 13. — Concentration of Hydrogen-Ion in Aqueous Solutions.* — Calculate the concentration of hydrogen-ion at  $25^\circ$ , *a*, in pure water; *b*, in 0.1 formal NaOH solution.

**105. The Hydrolysis of Salts.** — When either the acid or base of a salt has a very small ionization-constant, the salt in aqueous solution reacts with the water to an appreciable extent with formation of the acid and base. This phenomenon is called hydrolysis; and the fraction of the salt hydrolyzed is called the degree of hydrolysis, or simply the *hydrolysis* (*h*). Thus, at  $25^\circ$  in 0.01 formal solution potassium cyanide

and ammonium cyanide are hydrolyzed to the extent of 4.4 percent and 51.3 percent, respectively, according to the reactions:



As is done in the preceding chemical equations, it is convenient to indicate largely ionized substances, whose ionization is unknown and as an approximation may be assumed to be complete, by attaching + and - signs to their ions, and to indicate slightly ionized substances, whose ionization conforms to the mass-action law, by omitting these signs.

The hydrolysis of salts can be experimentally determined by a variety of methods. It may be derived from measurements of the conductance of the salt, as in Prob. 35 of Art. 77, and in Prob. 14 below; also from the effect of the salt on the rate of reactions whose rates are proportional to the concentration of hydroxide-ion or hydrogen-ion in the solution, as in Prob. 12 of Art. 85 and in Prob. 15 below. It may also be determined by measuring the distribution of the slightly ionized acid or base of the salt into an organic solvent, as in Prob. 16 below.

*Prob. 14. — Determination of Hydrolysis by Conductance Measurements.* — The specific conductance at  $100^\circ$  of a 0.025 formal solution of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  (ammonium acetate) is 0.00685 reciprocal ohms; and that of a second solution 0.025 formal in  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  and 0.025 formal in  $\text{NH}_4\text{OH}$  is 0.00717 reciprocal ohms. Calculate the hydrolysis of the ammonium acetate in the first solution, assuming that in the second solution the hydrolysis of the salt has been reduced to zero by the excess of base present and that the ionization and conductance of the base in the presence of its neutral salts are negligible.

*Prob. 15. — Determination of Hydrolysis by Reaction-Rate Experiments.* — The specific reaction-rate at  $100^\circ$  of the sugar hydrolysis has been found to be 0.0386 in a solution 0.001 formal in  $\text{HCl}$ , and to be 0.0946 in a solution 0.01 formal in  $\text{AlCl}_3$ . Calculate the fraction of the salt that is hydrolyzed (into  $\text{Al}(\text{OH})_3$  and  $3\text{HCl}$ ).

*Prob. 16. — Determination of Hydrolysis by Distribution Experiments.* — A 0.05 volume-formal solution of  $\text{Na}_2\text{NH}_4\text{PO}_4$  in water is found to be in equilibrium with a 0.00173 volume-formal solution of  $\text{NH}_3$  in chloroform at  $18^\circ$ . Calculate the hydrolysis of the salt into  $\text{NH}_4\text{OH}$  and  $\text{Na}^+{}_2\text{HPO}_4^-$ . The distribution-ratio for  $\text{NH}_3$  between water and chloroform at  $18^\circ$  is 27.5.

The equilibrium-constant of a hydrolytic reaction is called the *hydrolysis-constant*  $K_h$  of the salt. Thus the hydrolysis-constants of

potassium cyanide and ammonium cyanide are given by the expressions:

$$K_H = \frac{(\text{OH}^-)(\text{HCN})}{(\text{CN}^-)}; \text{ and } K_H = \frac{(\text{NH}_4\text{OH})(\text{HCN})}{(\text{NH}_4^+)(\text{CN}^-)}.$$

In evaluating these constants the largely ionized substances may as an approximation be regarded as completely ionized, as is to be done in the problems throughout this chapter. It will be noted that the error made in assuming complete ionization of the potassium cyanide and potassium hydroxide is largely eliminated, since these two substances are probably not far from equally ionized and since their concentrations occur as a ratio in the expression for the hydrolysis-constant. A similar compensation of the errors arising from the assumption of complete ionization is frequent in mass-action formulations. It will be seen, however, that such a compensation does not take place in the hydrolysis-constant of the ammonium cyanide when this is evaluated under the assumption that it is completely ionized; but even in this case, when this constant is used conversely for calculating hydrolysis (as in Prob. 17c) the error is small so long as the concentration of the salt is not greatly different from that for which the constant was evaluated.

Just as the equilibrium-constant of a metathetical gas reaction is determined by the dissociation-constants of the compounds present (Art. 101), so the equilibrium-constant for any reaction between ionized substances in solution is determined by the ionization-constants of the partially ionized substances involved. Accordingly, the hydrolysis-constant of a salt is determined (as shown in Prob. 18) by the ionization-constant  $K_w$  of water and the ionization-constants  $K_A$  and  $K_B$  of the slightly ionized acid and base produced. The hydrolysis of salts can therefore be calculated from these ionization-constants (as in Prob. 19); and conversely, these ionization-constants can be derived from experimentally determined values of the hydrolysis (as in Prob. 20).

*Prob. 17. — The Hydrolysis-Constant in Relation to the Hydrolysis. —*  
*a.* Calculate from the data in the above text the value of the hydrolysis-constant at 25° for KCN, and for  $\text{NH}_4\text{CN}$ . *b.* Formulate a general expression showing how the hydrolysis  $h$  of the salt varies with its concentration  $c$  in the case of KCN, and of  $\text{NH}_4\text{CN}$ . *c.* Calculate the hydrolysis of  $\text{NH}_4\text{CN}$  in a solution 0.01 formal in  $\text{NH}_4\text{CN}$  and 0.01 formal in  $\text{NH}_4\text{OH}$  at 25°.

*Prob. 18. — The Hydrolysis-Constant in Relation to the Ionization-Constants. — a.* Calculate the values of the hydrolysis-constant at  $25^\circ$  for KCN and for  $\text{NH}_4\text{CN}$  from the ionization-constants involved. *b.* Formulate general expressions for the relation between the hydrolysis-constant  $K_H$  of salts, like KCN and  $\text{NH}_4\text{CN}$ , and the ionization-constants  $K_w$ ,  $K_A$ ,  $K_B$ .

*Prob. 19. — Calculation of Hydrolysis from the Ionization-Constants. — a.* Calculate the concentrations of  $\text{NH}_4\text{OH}$ ,  $\text{H}^+$ , and  $\text{OH}^-$ , in a 0.1 f.  $\text{NH}_4\text{Cl}$  solution at  $25^\circ$  from the ionization-constants. *b.* Calculate the hydrolysis of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  in 0.025 formal solution at  $25^\circ$  from the ionization-constants.

*Prob. 20. — Calculation of the Ionization of Water from the Hydrolysis of Salts. —* Calculate the ionization-constant of water at  $100^\circ$  from the hydrolysis of  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  as determined in Prob. 14 and from the ionization-constants of  $\text{NH}_4\text{OH}$  and  $\text{HC}_2\text{H}_3\text{O}_2$  at  $100^\circ$ , which have been found by conductance measurements to be  $1.4 \times 10^{-6}$  and  $1.1 \times 10^{-5}$ , respectively.

**106. Ionization of Dibasic Acids and Their Acid Salts.** — Polybasic acids ionize in stages; thus, a dibasic acid  $\text{H}_2\text{A}$  ionizes according to the equations  $\text{H}_2\text{A} = \text{H}^+ + \text{HA}^-$  and  $\text{HA}^- = \text{H}^+ + \text{A}^-$ . The equilibrium-constants  $K_1$  and  $K_2$  of these reactions are called the ionization-constants for the first hydrogen and for the second hydrogen, respectively. The values of  $K_2$  are commonly much smaller than those of  $K_1$ . The values at  $25^\circ$  of the two constants for some important acids are given in the following table.

IONIZATION-CONSTANTS OF POLYBASIC ACIDS

Acid	$K_1$	$K_2$	$K_3$
$\text{H}_2\text{SO}_3$	$1.7 \times 10^{-2}$	$5 \times 10^{-6}$	—
$\text{H}_3\text{PO}_4$	$1 \times 10^{-2}$	$2 \times 10^{-7}$	$10^{-12}$
$\text{H}_2\text{C}_4\text{H}_4\text{O}_6$ (tartaric)	$9.7 \times 10^{-4}$	$4 \times 10^{-5}$	—
$\text{H}_2\text{CO}_3$	$3 \times 10^{-7}$	$6 \times 10^{-11}$	—
$\text{H}_2\text{S}$	$9 \times 10^{-8}$	$8 \times 10^{-16}$	—

\*From the two ionization-constants of a dibasic acid and its formal concentration  $c$  the concentrations of the various substances  $\text{H}_2\text{A}$ ,  $\text{HA}^-$ ,  $\text{A}^-$ , and  $\text{H}^+$  present in its solution can be calculated. In solving such mass-action problems involving many substances, the best plan is to formulate first the equilibrium equations that must be satisfied — thus, in this case the equations  $(\text{H}^+)(\text{HA}^-) = K_1(\text{H}_2\text{A})$  and  $(\text{H}^+)(\text{A}^-) = K_2(\text{HA}^-)$ . The next step is to formulate the so-called condition equations, which sum up the concentrations of the separate forms in which an element or other constituent exists in the solution.

Thus, in this case, for the total molal concentration  $\Sigma(A)$  of the constituent A, and for that  $\Sigma(H)$  of the hydrogen, we have:

$$\begin{aligned} (H_2A) + (HA^-) + (A^-) &= \Sigma(A) = c, \\ (H^+) + (HA^-) + 2(H_2A) &= \Sigma(H) = 2c. \end{aligned}$$

(It will be noted that one of these equations might be replaced by a simpler condition-equation of another kind; namely, by the equation,  $(H^+) = (HA^-) + 2(A^-)$ , which expresses the fact that positive and negative ions must be present in equivalent quantities.) We now have four independent equations containing four unknown concentrations. An exact algebraic solution of these equations is therefore possible. But, as such a solution is often very complicated, it is advisable to try first to simplify the condition-equations, which can often be done by neglecting in them the concentration of some substance which is small in comparison with the concentrations of each of the other substances occurring in the same equation. Thus, in this case the concentration  $(A^-)$  is small compared with the concentration  $H_2A$  because even the first hydrogen is split off to only a moderate extent, and it is small compared with the concentration  $(HA^-)$  for the reasons that  $K_2$  is small in comparison with  $K_1$  and that the hydrogen-ion produced by the ionization of the  $H_2A$  into  $H^+$  and  $HA^-$  further decreases by the common-ion effect the ionization of the  $HA^-$ . It is always well to test the correctness of such simplifying assumptions by subsequent calculation of the quantity neglected.

*\*Prob. 21. — Concentrations of the Substances Present in the Solution of a Dibasic Acid.* — From the ionization-constants given in the table above, calculate by the method just described the molal concentration of each of the substances present in a 0.01 formal solution of tartaric acid at 25°.

*\*Prob. 22. — Determination of the Ionization-Constant for the Second Hydrogen by Reaction-Rate Measurements.* — By measuring the conductance of tartaric acid in 0.06–0.01 formal solution, where the ionization of the second hydrogen is negligible, the ionization-constant for the first hydrogen of the acid has been found to be 0.00097 at 25°. The hydrogen-ion concentration in a 0.1 formal solution of sodium hydrogen tartrate, NaHA, has been shown by its catalytic effect (in Prob. 22 of Art. 93) to be 0.00020 molal. From these data calculate the concentrations  $(A^-)$ ,  $(HA^-)$  and  $(H_2A)$ , and the ionization-constant for the second hydrogen of tartaric acid. (In this case no simplification of the condition-equations is admissible, other than the assumption that the salts NaHA and Na<sub>2</sub>A are completely ionized.) Tabulate the molal concentrations of all the substances present in the solution of the sodium hydrogen tartrate.

*Determination of the Ionization-Constant for the Second or Third Hydrogen of Acids by Distribution Experiments. —*

\**Prob. 23.* A 0.1 volume-formal solution of sodium hydrogen succinate in water is found by experiment to be in equilibrium at 25° with a 0.00187 volume-formal solution of succinic acid in ether. The distribution-ratio of succinic acid between water and ether at 25° is 7.5.  
*a.* Find the concentration of unionized succinic acid in the aqueous solution of the acid salt. *b.* Calculate the ionization-constant for the second hydrogen. That for the first hydrogen is  $6.6 \times 10^{-5}$ . Neglect the value of  $(H^+)$  in the condition-equation. *c.* Show by calculating the value of  $(H^+)$  that it was justifiable to neglect it. *Ans. b.*  $2.5 \times 10^{-6}$ .

\**Prob. 24.* Calculate the ionization-constant at 18° for the third hydrogen of  $H_3PO_4$  (that for the ion  $HPO_4^{2-}$ ) from the data of *Prob. 16* and from the ionization-constants of water and of ammonium hydroxide, which at 18° are  $0.5 \times 10^{-14}$  and  $1.7 \times 10^{-5}$ , respectively.

**107. Displacement of One Acid or Base from its Salt by Another. —**

One of the most important types of equilibrium in aqueous solution is the partial displacement of one acid or base from its salt by another; for example, that of acetic acid from sodium acetate by formic acid, or that of ammonium hydroxide from ammonium chloride by sodium hydroxide.

Before the mass-action relations involved were fully understood, the extent of the displacement was taken as a measure of the relative *strengths* of different acids or bases; those which are largely displaced from their salts being called weak acids or bases, and those which cause such displacement being called strong acids or bases. It is shown by *Probs. 25-28* that the mass-action law and ionic theory give a comparatively simple explanation of this phenomenon in the case of not largely ionized univalent acids or bases; also that the relative strengths of different acids or bases, as shown by their displacements, are determined by their ionization, weak ones being those which are slightly ionized and strong ones those which are largely ionized.

*Displacement of Acids or Bases from their Salts. —*

*Prob. 25.* — To a 0.1 formal solution of  $KNO_2$  is added at 25° an equal volume of a 0.1 formal solution of acetic acid. *a.* Calculate the fraction of the potassium nitrite that is converted into potassium acetate. *b.* Calculate the fraction that would be so converted if the acetic acid solution were 1.0 formal (instead of 0.1 formal).

*Prob. 26.* — *a.* For the general case expressed by the equation  $B^+A^- + HA' = B^+A'^- + HA$  where the solution is originally *c* formal in  $B^+A^-$  and *c'* formal in  $HA'$ , derive an expression for the fraction *x* of the salt  $B^+A^-$

converted into the salt  $B^+A'^-$ , assuming that the ionization-constants of both acids are so small that the ionization of them in the presence of their salts is negligible. *b.* Derive from this expression the relation between the ionization-constants of the acids and the fractions of the basic constituent that are combined with the two acidic constituents for the case that  $c = c'$ ; and state the principle fully in words.

*Prob. 27.* — To a liter of 0.1 formal HCl solution is added at 25° a liter of 0.1 formal  $NH_4OH$  solution and a liter of 0.1 formal  $CH_3NH_2OH$  solution. Calculate the fraction of the acid which combines with each base.

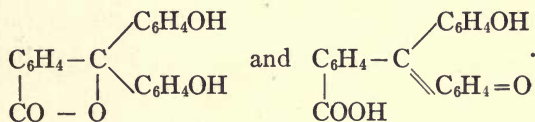
*Prob. 28.* — A 0.1 formal solution of acetic acid is added to an equal volume of 0.1 formal  $NaHCO_3$  solution at 25°, the carbon dioxide produced being kept above the solution at a pressure of 1 atm. *a.* Calculate the concentrations of the two salts and two acids in the resulting solution, taking 0.0338 as the solubility-constant (Art. 39) for  $CO_2$  in water at 25°. *b.* Repeat the calculation for the case where no carbon dioxide is allowed to escape from the solution; and tabulate the two results.

The displacement of acids and bases from their salts can often be determined by measuring the heat effect or the change in volume (as in Prob. 30) attending the addition of one acid to the salt of the other acid, or of one base to the salt of the other base. In cases where one of the acids has a color different from that of its salt (as in Prob. 29), the displacement can be determined by measuring the attendant color change.

*Prob. 29. — Determination of Displacement by Color Measurements.* — Violuric acid is a slightly ionized acid whose solution is colorless, while solutions of its salts have a violet color which increases proportionately with the quantity of salt. 25 ccm. of a 0.01 formal solution of violuric acid are placed in each of two tubes of the same diameter; to one tube are added 25 ccm. of a 0.01 formal solution of potassium acetate; and to the other tube is added 0.01 formal KOH solution until on looking down through the tubes the colors are seen to be the same, 13.75 ccm. of the KOH solution being required. *a.* Calculate the fraction of the violuric acid which exists in the first mixture in the form of its salt. *b.* Calculate the ionization-constant of the violuric acid.

\* *Prob. 30. — Determination of Displacement by Volume Measurements.* — When 1000 g. of a solution containing 1 KOH is mixed with 1000 g. of a solution containing 1  $HC_2H_3O_2$  there is an increase of volume of 9.52 ccm. When the former solution is mixed with 1000 g. of a solution containing 1  $HCHO_2$  there is an increase of volume of 12.39 ccm. When 2000 g. of a solution containing 1  $KCHO_2$  is mixed with 1000 g. of one containing 1  $HC_2H_3O_2$  there is a decrease of volume of 0.74 ccm. *a.* Determine what fraction of the formic acid is displaced from its salt by the acetic acid. *b.* Calculate from the ionization-constants the fraction displaced, and compare the results. *Ans. a,* 0.26.

**108. Neutralization-Indicators.** — An acid neutralization-indicator (such as litmus, paranitrophenol, or phenol phthalein) is a mixture of two isomeric acids ( $\text{HIn}'$  and  $\text{HIn}''$ ) in equilibrium with each other, one of which ( $\text{HIn}''$ ) is present in much smaller proportion, but is so much more ionized than the other ( $\text{HIn}'$ ) that when a base  $\text{BOH}$  is added the salt produced is almost wholly of the form  $\text{B}^+\text{In}''^-$ . The substances  $\text{HIn}'$  and  $\text{B}^+\text{In}''^-$  are different in color from the substances  $\text{HIn}''$  and  $\text{B}^+\text{In}''^-$ , the color being determined only by the molecular structure of the group  $\text{In}$ . It follows from these conditions that the indicator acid changes color when converted into its salt. For example, phenolphthalein exists in two isomeric forms to which the following molecular structures are assigned:



The first is the (colorless) form  $\text{HIn}'$  which is present in predominating proportion in acid solution; the second is the (red) form  $\text{HIn}''$ , which has a much larger ionization-constant, and hence on the addition of alkali is converted into its (red) salt in much larger proportion than the other form.

It can be shown by the mass-action law that the indicator behaves as if it were a single acid  $\text{HIn}$  whose salt has a different color from the acid itself; and its behavior can be represented by a single constant called the *indicator-constant*  $K_I$ . Namely, by combining the two equilibrium equations:

$$\frac{(\text{HIn}'')}{(\text{HIn}')} = K \quad \text{and} \quad \frac{(\text{H}^+) (\text{In}''^-)}{(\text{HIn}'')} = K'',$$

there results the equation

$$\frac{(\text{H}^+) (\text{In}''^-)}{(\text{HIn}')} = K K'' = K_I.$$

Since according to the above statements  $(\text{In}'^-)$  is negligible in comparison with  $(\text{In}''^-)$ , and  $(\text{HIn}'')$  is negligible in comparison with  $(\text{HIn}')$ , the total indicator acid is substantially equal to  $(\text{HIn}')$ , and the total indicator salt is substantially equal to  $(\text{In}''^-)$ . Hence in the above expression the ratio  $(\text{In}''^-)/(\text{HIn}')$  may be replaced by the ratio

$x/(1-x)$ , where  $x$  represents the fraction of the total quantity of the indicator which is in the colored form that exists in alkaline solution. Making this substitution, there results the following fundamental indicator equation:

$$(H^+) \frac{x}{1-x} = K_1.$$

The relations in the case of basic indicators (existing almost wholly in the two differently colored forms  $In'OH$  and  $In''+A^-$ ) are entirely similar to those in the case of acid indicators. By formulating the mass-action equations, it can, in fact, be shown that the relation just derived between the hydrogen-ion concentration and the fraction  $x$  of the indicator transformed holds true also in the case of basic indicators. A basic indicator may therefore be treated as an acid indicator by adopting as the value of its indicator-constant that calculated by the above-given indicator equation; and it will be so treated in the following problems.

*Prob. 31. — Determination of the Indicator-Constant.* — To 100 ccm. of a solution 0.1 normal in potassium acetate and 0.01 normal in acetic acid are added 10 ccm. of a 0.01 normal solution of paranitrophenol. This solution is found to have the same yellow color as a solution made by adding 0.50 ccm. of 0.01 normal paranitrophenol solution and 9.5 ccm. of 0.01 normal KOH solution to 100 ccm. of water. *a.* Calculate the indicator-constant, neglecting the quantity of the acetic acid displaced from its salt by the small proportion of paranitrophenol present. *b.* Show what percentage error is made in  $(H^+)$ , and therefore in  $K_1$  by neglecting this displaced quantity.

*Prob. 32. — Determination of Small Hydrogen-Ion Concentrations by Means of Indicators.* — When a small proportion of phenolphthalein ( $K_1 = 10^{-10}$ ) is added to a 0.1 formal solution of  $NaHCO_3$  at  $25^\circ$  the indicator is found by color comparisons to be 6.0% transformed into its salt. Calculate the hydrogen-ion and hydroxide-ion concentrations in the solution.

It is evident from the indicator equation that in the titration of an acid with a base an end-point will be reached when the hydrogen-ion concentration ( $H^+$ ) becomes so reduced that a considerable fraction  $x$  of the indicator is transformed into its salt; also that the observed end-point will be correctly located only if this transformation occurs when equivalent quantities of acid and base are present, and that the sharpness of the end-point will depend on how fast the hydrogen-ion concentration changes in this region. Hence, in order to determine how an acid of any known ionization-constant will behave on titration

and in order to select the most suitable indicator, it is necessary to know how the hydrogen-ion concentration varies when a largely ionized base is progressively added. The following table contains data of this kind, calculated as shown in Prob. 33. Namely, it shows the hydrogen-ion concentrations prevailing at  $25^\circ$  in solutions of acids of ionization-constants  $10^{-3}$ ,  $10^{-5}$ ,  $10^{-7}$ , and  $10^{-9}$  when the ratio  $B/A$  of the quantity of NaOH added to the quantity of the acid present has the values given in the first column (the original concentration of the acid and that of the standard base being 0.2 normal).

CHANGE OF THE HYDROGEN-ION CONCENTRATION ON NEUTRALIZATION

Ratio B/A	Values of the hydrogen-ion concentration for			
	$K_A = 10^{-3}$	$K_A = 10^{-5}$	$K_A = 10^{-7}$	$K_A = 10^{-9}$
0.980	$2 \times 10^{-5}$	$2 \times 10^{-7}$	$2 \times 10^{-9}$	$2.4 \times 10^{-11}$
0.990	$1 \times 10^{-5}$	$1 \times 10^{-7}$	$1 \times 10^{-9}$	$1.6 \times 10^{-11}$
0.995	$5 \times 10^{-6}$	$5 \times 10^{-8}$	$5 \times 10^{-10}$	$1.2 \times 10^{-11}$
0.998	$2 \times 10^{-6}$	$2 \times 10^{-8}$	$2.4 \times 10^{-10}$	$1.1 \times 10^{-11}$
1.000	$1 \times 10^{-8}$	$1 \times 10^{-9}$	$1 \times 10^{-10}$	$1.0 \times 10^{-11}$
1.002	$5 \times 10^{-11}$	$5 \times 10^{-11}$	$4 \times 10^{-11}$	$0.9 \times 10^{-11}$
1.005	$2 \times 10^{-11}$	$2 \times 10^{-11}$	$2 \times 10^{-11}$	$0.8 \times 10^{-11}$
1.010	$1 \times 10^{-11}$	$1 \times 10^{-11}$	$1 \times 10^{-11}$	$0.6 \times 10^{-11}$
1.020	$5 \times 10^{-12}$	$5 \times 10^{-12}$	$5 \times 10^{-12}$	$0.4 \times 10^{-11}$

These numbers are also the values of the hydroxide-ion concentration for the case that a 0.2 normal solution of a base having an ionization-constant equal to  $10^{-3}$ ,  $10^{-5}$ ,  $10^{-7}$ , or  $10^{-9}$  is titrated with a 0.2 normal solution of a strong acid (like HCl), provided the numbers in the first column denote the ratio (A/B) of the quantity of acid to the quantity of base. Thus, when the ratio A/B is 0.98, the value of  $(OH^-)$  is  $2 \times 10^{-5}$  for a base for which  $K = 10^{-3}$ .

#### *Titration of Acids and Bases. —*

*Prob. 33.* — 100 ccm. of a 0.2 normal solution of an acid whose ionization-constant is  $10^{-5}$  are titrated at  $25^\circ$  with 0.2 normal KOH solution. Calculate the hydrogen-ion concentration ( $H^+$ ) in the mixture when 99.0, 99.5, 99.8, 100.0, 100.2, 100.5, and 101.0 ccm. of the KOH solution have been added, using  $1 \times 10^{-14}$  as the ionization-constant of water.

*Prob. 34.* — *a.* Plot the common logarithms of the values of the hydrogen-ion concentrations given in the preceding table as ordinates against the corresponding values of the ratio of base to acid as abscissas, for each of the four acids. *b.* On the right-hand side of the same diagram write in a scale of values of  $\log_{10}(OH^-)$  corresponding to the values of  $\log_{10}(H^+)$  on the left-hand side; and at the top of the diagram write in a scale of ratios of acid to base (A/B) corresponding to the

scale of ratios of base to acid at the bottom (thus,  $B/A = 0.98$  corresponds to  $A/B = 1.02$ ). Now make plots on the same diagram, showing how  $(H^+)$  or  $(OH^-)$  varies in titrating bases of ionization-constants  $10^{-3}$ ,  $10^{-5}$ ,  $10^{-7}$ , and  $10^{-9}$  with HCl at  $25^\circ$ , similar in all respects to the plots previously made for the four acids.

*Prob. 35.* — *a.* From a study of the diagram of *Prob. 34* tabulate the values between which the indicator-constant must lie in order that the titration of each of the four acids and four bases may be correct within 0.2%, assuming that the indicator is 9% transformed. *b.* Show from the plot what percentage error would be made in using phenolphthalein ( $K_I = 10^{-10}$ ) in titrating an acid for which  $K_A = 10^{-5}$  when the fraction of the indicator transformed is 1%, 9%, and 50%; also in titrating an acid for which  $K_A = 10^{-7}$  when the fraction of the indicator transformed is 9% and 50%. *c.* If the acid for which  $K_A = 10^{-9}$  were titrated with the aid of an indicator for which  $K_I = 10^{-12}$  (which is not far from the value for trinitrobenzene), what error would be made when the fraction of the indicator transformed is 5%, 9%, and 15%? (Note that in a titration carried out in the usual way the fraction transformed is not determined more closely than this. Note also that an error in the assumed value of the indicator-constant would affect the results in the same way as a variation in the fraction transformed.)

*Prob. 36.* — Calculate the value of  $(H^+)$  at the end-point in titrating with phenolphthalein ( $K_I = 10^{-10}$ ) when the fraction  $x$  of it transformed is 5% and 20%; with rosolic acid ( $K_I = 10^{-8}$ ) when  $x$  is 5% and 20%; with paranitrophenol ( $K_I = 10^{-7}$ ) when  $x$  is 1% and 20%; and with methyl orange ( $K_I = 5 \times 10^{-4}$ ) when  $x$  is 80% and 95% (these being about the ranges practicable in a titration). Draw in on the diagram made in *Prob. 34* horizontal lines representing these limiting values of  $(H^+)$  for the four indicators. Letter the curves and lines on the diagram so as to show what each represents.

*Prob. 37.* — With the aid of the diagram show which of these indicators would give a result accurate within 0.2–0.3% in titrating *a*,  $NH_4OH$  with HCl; *b*,  $HNO_2$  with KOH; *c*, aniline ( $C_6H_5NH_2$ ) with HCl.

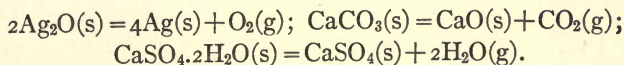
*Prob. 38.* — *Titration of the Successive Hydrogens of Polybasic Acids.* — A solution 0.2 formal in  $H_3PO_4$  is titrated with 0.2 formal NaOH solution. With the aid of the ionization-constants, calculate the  $H^+$  ion concentration after the addition of enough base to be equivalent, *a*, to 99% of the first hydrogen of the acid, *b*, to 1% of the second hydrogen, *c*, to 99% of the second hydrogen, and *d*, to 1% of the third hydrogen. *e.* By reference to the diagram determine what indicators could be used for titrating the first hydrogen and the second hydrogen of the acid.

## IV. THE MASS-ACTION LAW FOR REACTIONS INVOLVING SOLID PHASES

**109. Form of the Mass-Action Expression.** — When a substance present as a solid phase is involved in a reaction with gaseous substances at small pressures, that substance has in the gaseous phase of all equilibrium mixtures at any definite temperature the same pressure, namely, one equal to the vapor-pressure of the solid substance. Similarly, when a substance present as a solid phase is involved in a reaction with dissolved substances at small concentrations, it has in the liquid phase of all equilibrium mixtures at any definite temperature the same concentration, namely, one equal to its concentration in a solution saturated with the solid substance and containing no other solutes. Hence the pressure in the gaseous phase or the concentration in the liquid phase of any substances which are also present as solid phases may be left out in formulating the mass-action expression; their constant pressures or concentrations being understood to be included in the equilibrium-constant. Thus,  $p_{\text{H}_2}/p_{\text{H}_2\text{O}} = K$  is the mass-action expression for the reaction  $\text{Fe(s)} + \text{H}_2\text{O(g)} = \text{FeO(s)} + \text{H}_2\text{(g)}$ .

As here illustrated, solid, liquid, and gaseous substances occurring in chemical equations are indicated by attaching to their formulas (s), (l), and (g), respectively, when it is important to show the state of aggregation. Substances in solution are written either without any such addition to their formulas or with the addition of a parenthesis showing the concentration or composition; for example,  $\text{NH}_3$  (0.1 f.),  $\text{H}^+\text{Cl}^-$  (in 100  $\text{H}_2\text{O}$ ).

**110. Reactions involving Solid and Gaseous Substances.** — The simplest type of the reactions involving solid and gaseous substances is that in which only one substance is present in appreciable quantity in the gaseous phase. Examples of this type are:



The mass-action expression for this case is simply  $p = K$ , which signifies that at any definite temperature there is only one pressure of the gas at which there can be equilibrium. This pressure is called the *dissociation-pressure* of the substance undergoing decomposition (thus of the silver oxide, the calcium carbonate, or the gypsum). If the pressure of the gas is kept larger than this pressure, the reaction takes place completely in one direction, with the result that the gas is entirely absorbed; and if the pressure is kept smaller, the reaction

takes place completely in the other direction, with the result that the dissociating substance completely decomposes. This important characteristic of reactions of this type will be fully considered in Art. 119.

Other types of reactions, involving equilibrium between solid substances and two or more gaseous substances, are illustrated by the following problems.

*Dissociation of Solid Substances Producing Two Gaseous Substances. —*

*Prob. 39.* — When solid  $\text{NH}_4\text{SH}$  is placed in a vacuous space at  $25^\circ$  a pressure of 500 mm. is developed, owing to the dissociation of the salt, which is itself not appreciably volatile, into  $\text{NH}_3$  and  $\text{H}_2\text{S}$ . If solid  $\text{NH}_4\text{SH}$  were introduced into a space which already contained  $\text{H}_2\text{S}$  at a pressure of 300 mm., what increase of pressure would result?

*Prob. 40.* — The equilibrium-constant (expressed in atmospheres) of the reaction  $2\text{NaHCO}_3(\text{s}) = \text{Na}_2\text{CO}_3(\text{s}) + \text{CO}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$  at  $100^\circ$  is 0.23. A current of moist carbon dioxide is passed at 1 atm. over solid sodium hydrogen carbonate (in order to free it from adhering water). How great must the mol-fraction of the water in the gas be to prevent decomposition of the salt?

*Prob. 41.* — When solid mercuric oxide is heated in an evacuated tube to  $357^\circ$  in the vapor of mercury boiling at 1 atm., a pressure of 70 mm. is produced in the tube owing to dissociation of the oxide into mercury vapor and oxygen. Assuming that a mixture of solid mercuric oxide and liquid mercury is heated in the same way, calculate the partial pressure of the oxygen in the tube. *Ans.* 0.088 mm.

*Prob. 42.* — *Equilibrium of the Producer Gas Reaction.* — In one stage of the manufacture of producer gas a current of air at 1 atm. is passed through coke at a high temperature. Calculate the mol-fractions of  $\text{CO}_2$  and of  $\text{CO}$  in the gas issuing at  $1000^\circ$ , assuming equilibrium to be reached. The equilibrium-constant for the reaction  $\text{C}(\text{s}) + \text{CO}_2(\text{g}) = 2\text{CO}(\text{g})$  at  $1000^\circ$  is 140.

*Dissociation-Pressure in Relation to Equilibrium-Constants. —*

*Prob. 43.* — At  $1120^\circ$  the gaseous mixture in equilibrium with iron and ferrous oxide consists of 54 mol-percent of  $\text{H}_2$  and 46 mol-percent of  $\text{H}_2\text{O}$ . Calculate the dissociation-pressure of ferrous oxide, referring to Prob. 8 for the additional data needed.

*Prob. 44.* — In the blast-furnace process iron is reduced by the reaction  $\text{FeO}(\text{s}) + \text{CO}(\text{g}) = \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$ . Calculate the least quantity of carbon monoxide that could reduce one formula-weight of  $\text{FeO}$  at  $1120^\circ$ , using the dissociation-pressure of ferrous oxide found in Prob. 43.

**111. Solubility of Unionized and Slightly Ionized Substances. —** The fundamental principle determining the solubility of a unionized or slightly ionized substance in the presence of other solutes is that the concentration of this substance, or of its unionized part if its

ionization is not negligible, has the same value at any definite temperature in any solution saturated with respect to this substance, whatever other solutes may be present at small concentrations. The application of this principle is illustrated by the following problems.

*Solubility-Increase Due to Complex Formation. —*

*Prob. 45.* — At  $25^{\circ}$  the solubility of iodine in water is 0.0013 molal, and its solubility in 0.1 formal KI solution is 0.0517 molal, the increase being due to the reaction  $K^+I^- + I_2(s) = K^+I_3^-$ . Calculate its solubility in 0.01 formal KI solution at  $25^{\circ}$ .

*Prob. 46* — Calculate the solubility of  $HgCl_2$  in 0.1 formal NaCl solution at  $25^{\circ}$  from the results of the distribution experiments of Prob. 44 of Art. 45 and from the fact that its solubility in water at  $25^{\circ}$  is 0.263 molal.

**112. Solubility of Largely Ionized Substances.** — The mass-action law evidently requires, in all dilute solutions saturated with the same solid substance, that the concentration of the unionized substance have the same value, and also that the product of the ion-concentrations raised to the appropriate power have the same value, whatever other substances may be present (at small concentrations). Thus at any definite temperature in any aqueous solution saturated with silver sulfate, whether it is present alone or with another solute, such as silver nitrate or ammonium hydroxide, the first of these principles requires that  $(Ag_2SO_4)$  have a definite value; and the second principle requires that the product  $(Ag^+)^2 \times (SO_4^{--})$  also have a definite value. This saturation value of the ion-concentration product is commonly called the *solubility-product*; and the principle expressing its constancy is called the *solubility-product principle*.

The principle relating to the concentration of the unionized part cannot be applied to largely ionized substances; for the degree of ionization of such substances is so imperfectly known that it is not possible to estimate even roughly the concentration of the unionized part. In the case of largely ionized substances the solubility-product principle is therefore employed; but even this gives only approximate results, since, as shown in Art. 103, ions deviate considerably from the laws of perfect solutions even at fairly small concentrations. Nevertheless, the solubility-product principle, supplemented by the hypotheses that largely ionized substances are completely ionized and that their ions act as perfect solutes, yields roughly approximate results in the treatment of the solubility effects of uniunivalent substances up to moderate concentrations, such as 0.1–0.2 formal, as

will be shown in the following problems by comparison of the observed solubility values with those calculated from the solubility in pure water. The effects of uniunivalent substances on the solubility of unibivalent substances, and the effects of unibivalent substances on the solubility of uniunivalent substances, are also in roughly approximate agreement with the requirements of these principles. Very large deviations are met with, however, in evaluating the solubility of one unibivalent substance in the presence of another. Thus the effect of  $\text{Ag}^+\text{NO}_3^-$  on the solubility of  $\text{Ag}_2\text{SO}_4^-$ , or the effect of  $\text{Ca}^{++}\text{Cl}^-$  on the solubility of  $\text{TI}^+\text{Cl}^-$ , may be estimated by these principles; but the effect of  $\text{Na}_2\text{SO}_4^-$  on the solubility of  $\text{Ag}_2\text{SO}_4^-$  is very different from that calculated. This very abnormal effect exerted by bivalent ions may arise either from great deviations in their behavior from that of perfect solutes, or from their conversion into intermediate ions (such as  $\text{AgSO}_4^-$  in the case of  $\text{Ag}_2\text{SO}_4$ ). In view of this great divergence it is not practicable to predict even approximately the effect of unibivalent salts on the solubility of one another, except at very small concentrations (for example, below 0.01 formal).

An exact method of treatment of solubility effects in the case of largely ionized substances is described in Art. 113.

*Solubility-Decrease by Substances with a Common Ion. —*

*Prob. 47.* — The solubility of  $\text{AgBrO}_3$  in water at  $25^\circ$  is 0.0081 formal. Calculate its solubility in a solution 0.0085 formal in  $\text{AgNO}_3$ , and compare the result with the value 0.0051 formal experimentally determined.

*Prob. 48.* — The solubility of  $\text{KClO}_4$  in water at  $25^\circ$  is 0.148 formal. Calculate its solubility in a solution 0.100 formal in  $\text{KCl}$ . Compare the result with the value 0.112 formal experimentally determined.

*Prob. 49.* — *a.* Derive an expression for the solubility  $s$  of  $\text{AgCl}$  in a dilute  $\text{NaCl}$  solution of concentration  $c$  in terms of its solubility  $s_0$  in water. *b.* Calculate the ratio  $s/s_0$  for  $c = s_0$ , for  $c = 2s_0$ , and  $c = 10s_0$ .

*Prob. 50.* — The solubility of  $\text{Ag}_2\text{SO}_4$  in water at  $25^\circ$  is 0.0268 formal. Calculate its solubility,  $a$ , in a solution 0.050 formal in  $\text{AgNO}_3$ ,  $b$ , in a solution 0.025 formal in  $\text{K}_2\text{SO}_4$ , solving in each case the cubic equation by trial. *c.* Tabulate the results with those actually determined, which are 0.0142 and 0.0247, respectively.

*Prob. 51.* — The solubility of  $\text{Mg}(\text{OH})_2$  in water at  $18^\circ$  is  $1.4 \times 10^{-4}$  formal. *a.* Calculate its solubility in 0.002 formal  $\text{NaOH}$  solution. *b.* Calculate its solubility in 0.001 formal  $\text{MgCl}_2$  solution.

*Prob. 52.* — *Solubility-Increase through Metathesis.* — The solubility of  $\text{Mg}(\text{OH})_2$  in water at  $18^\circ$  is  $1.4 \times 10^{-4}$  formal. *a.* Calculate its solubility in 0.002 formal  $\text{NH}_4\text{Cl}$  solution. Neglect the concentration

of  $\text{OH}^-$  in comparison with that of  $\text{NH}_4\text{OH}$ . *b.* Calculate the ratio of  $(\text{OH}^-)$  to  $(\text{NH}_4\text{OH})$  in the saturated solution in order to test the simplifying assumption above made. *Ans. a,*  $8.6 \times 10^{-4}$ .

*Prob. 53. — Solubility-Increase through Complex-Formation. —* The solubility of  $\text{AgCl}$  in water at  $25^\circ$  is  $1.30 \times 10^{-5}$  formal. Calculate its solubility in 0.1 formal  $\text{NH}_3$  solution. There is formed a complex ion by the reaction  $\text{Ag}^+ + 2\text{NH}_3 = \text{Ag}(\text{NH}_3)_2^+$ , its equilibrium-constant (commonly called the complex-constant) having the value  $1.4 \times 10^7$ . *Ans. 0.0044.*

*Conversion of One Solid Substance into Another. —*

*Prob. 54. —* The solubility of silver thiocyanate is  $1.2 \times 10^{-6}$  formal and that of silver bromide is  $0.7 \times 10^{-6}$  formal at  $25^\circ$ . *a.* Calculate the equilibrium-constant of the reaction  $\text{AgSCN}(s) + \text{K}^+\text{Br}^- = \text{AgBr}(s) + \text{K}^+\text{SCN}^-$  in dilute solution. *b.* If 8.3 g. of solid  $\text{AgSCN}$  are treated with 200 ccm. of 0.1 formal  $\text{KBr}$  solution, what proportion of the silver salt is converted into bromide? *c.* What volume of the 0.1 formal  $\text{KBr}$  solution would convert the solid  $\text{AgSCN}$  completely into  $\text{AgBr}$ ? *d.* With what mixtures of potassium thiocyanate and potassium bromide could the silver thiocyanate be treated without any change taking place?

*Prob. 55. —* Determine the ratio of carbonate to hydroxide in the solution obtained by digesting at  $25^\circ$  a 0.1 formal  $\text{Na}_2\text{CO}_3$  solution with excess of solid  $\text{Ca}(\text{OH})_2$  (as in the technical process of causticizing soda). The solubility of calcium hydroxide is 0.020 formal, and the product  $(\text{Ca}^{++}) \times (\text{CO}_3^{--})$  has the value  $3 \times 10^{-9}$  in water saturated with calcium carbonate.

**\*113. The Mass-Action of Imperfect Solutes. The Concept of Activity. —** The mass-action law is a limiting law rigorously exact only for perfect gases or perfect solutes, but holding true with reasonable accuracy in the case of most gases at moderate pressures (such as 1 to 5 atmospheres), and in the case of solutes with electrically neutral molecules up to moderate concentrations (such as 1 molal), but showing large deviations in the case of ions even at small concentrations (such as 0.1 molal). For the mass-action and thermodynamic treatment of solutes at concentrations larger than those at which they can be regarded as perfect solutes, it has been found convenient to introduce a new concept, which will now be described.

The mass-action of a perfect gas or perfect solute, as the mass-action law states, is represented by its concentration; but when a chemical substance is not a perfect gas or solute or when its concentration is unknown, its mass-action is expressed by the term *activity* ( $a$ ), by which is meant that quantity which, when substituted for the concentration of the substance in mass-action equations, expresses

its effect in determining the equilibrium. Hence the activity of a substance represents its effective concentration from a mass-action viewpoint; and the factor by which the actual concentration  $c$  must be multiplied to give the activity is called the *activity-coefficient*  $\alpha$ , that is,  $a = \alpha c$ , or  $\alpha = a/c$ .

In accordance with these general definitions, the most obvious method of determining the relative activities of a substance in two solutions of different concentrations, or in general in any two phases, is to find its concentrations in gaseous phases in equilibrium with the two solutions, or in general with the two phases; for the activity of a perfect gas is placed equal to its concentration, and the activity of a gas at small pressure can ordinarily be considered to be substantially equal to its concentration. This method affords a definition of activity, which is more specific and quantitative than the general statement in regard to it made above. Namely, the ratio of the *activities* of a substance in two phases is equal to the ratio of its vapor-pressures in the two phases, provided the vapor can be regarded as perfect gas. That is,  $a_1/a_2 = p_1/p_2$ . For example, the ratio of the activities of unionized hydrochloric acid in its 10 formal and 7 formal aqueous solutions at 25° is 30.0, since the partial vapor-pressures of the hydrochloric acid in those solutions have been found to be 4.2 and 0.14 mm. of mercury. This quantity is also the ratio of the products of the activities of hydrogen-ion and chloride-ion in the two solutions, since these products are by definition the quantities that must be substituted in the mass-action expression for the equilibrium of the reaction  $\text{HCl} = \text{H}^+ + \text{Cl}^-$ . These statements are expressed by the equations:

$$\frac{(p_{\text{HCl}})_1}{(p_{\text{HCl}})_2} = \frac{(a_{\text{HCl}})_1}{(a_{\text{HCl}})_2} = \frac{(a_{\text{H}^+})_1 (a_{\text{Cl}^-})_1}{(a_{\text{H}^+})_2 (a_{\text{Cl}^-})_2}$$

*Calculation of Activity Ratios from Vapor-Pressure. —*

*Prob. 56. — a.* Calculate the relative activities of  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in 1.0 formal and in 0.1 formal solution at 25° from the facts that the vapor-pressures of  $\text{NH}_3$  in these solutions are 13.52 mm. and 1.334 mm., and that the vapor-pressures of  $\text{H}_2\text{O}$  are those required by Raoult's law. *b.* Calculate the ratio of the activities of the  $\text{NH}_4\text{OH}$  in these two solutions; also the ratio in each solution of the activity of the  $\text{NH}_4\text{OH}$  to that of the  $\text{NH}_3$ . *c.* Calculate the ratio of the products of the activities of the  $\text{NH}_4^+$  and  $\text{OH}^-$  ions in the two solutions.

*Prob. 57. — a.* Calculate the ratio of the activities of  $\text{H}_2\text{O}$  in pure water and in 1 formal  $\text{NaCl}$  solution at 0°, whose mol-number (Art. 59)

is 1.79, as determined from its freezing-point. *b.* Find also the ratio of the product of the activities of the  $H^+$  and  $OH^-$  ions in pure water to the product in 1 formal NaCl solution at  $0^\circ$ .

This direct method is of very limited applicability to largely ionized substances, since they seldom have appreciable vapor-pressures. There is, however, a simple thermodynamic relation between activity and electromotive force (considered in Arts. 146 and 147) which furnishes a means of determining the change in the product of the activities of the ions with the concentration of the salt; and, by assuming that at very small concentrations the activity of the ions is equal to the concentration of the ion-constituent, absolute values of the product of the activities of the ions at various concentrations of the substance are obtained. The change in the activity of solutes with the concentration can also be derived from the freezing-point lowering with the aid of thermodynamic relations, and from the effect of salts on the solubility of one another.

A number of substances have already been studied by these methods. The following table contains some typical values of the activity-coefficient at  $25^\circ$ . (These values are in reality the square-root of the product of the activity-coefficients of the two ions of the substance, or the geometrical mean of the activity-coefficients of the two ions; for it is only this product that can be determined.) These values are so expressed as to be the quantity by which the concentration of the substance must be multiplied to give the activity of the ions. For comparison the values of the conductance-viscosity ratio are also given in the table. Potassium chloride and ammonium chloride have been found to have substantially the same activity-coefficients and the same conductance-viscosity-ratios as sodium chloride, at any rate up to 0.2 formal.

ION-ACTIVITY COEFFICIENTS

Formality	Ion-Activity-Coefficients				Conductance-Viscosity-Ratios			
	NaCl	LiCl	HCl	KOH	KCl	LiCl	HCl	KOH
0.001	0.98	0.98	0.99	—	0.98	0.98	0.99	0.99
0.010	0.92	0.92	0.92	0.92	0.94	0.93	0.97	0.96
0.020	0.89	0.89	0.89	0.89	0.93	0.92	0.96	0.95
0.050	0.84	0.84	0.86	0.84	0.89	0.88	0.94	0.92
0.100	0.80	0.80	0.81	0.80	0.86	0.85	0.92	0.91
0.200	0.75	0.77	0.78	0.75	0.83	0.81	0.91	0.89
0.500	0.69	0.75	0.76	0.73	0.78	0.77	0.89	0.88
1.000	0.65	0.78	0.82	0.75	0.74	0.74	0.84	0.88
3.000	0.70	1.20	1.35	1.1	—	—	—	—

The table shows that with increasing concentration the ion-activity-coefficient of all four substances decreases at first much more rapidly than the conductance-viscosity-ratio. Thus at 0.1 formal the coefficient is less than this ratio by 6 to 12 percent. Moreover, the coefficient, unlike the ratio, passes through a minimum at about 0.5 formal (except in the case of sodium chloride where the minimum occurs between 1 and 3 formal). This comparison shows quantitatively the error in assuming that the conductance-viscosity-ratio is a measure of the ion-activity.

The activity-coefficient, however, does not show, any more than the conductance-ratio, the ionization of the substance. For just as the conductance-ratio affords no means of determining the separate influences of ionization and ion-mobility, so these activity-coefficients do not show to what extent the change of activity with increasing concentration is due to decreasing ionization and to what extent it is due to an increasing deviation in the behavior of the ions from that of perfect solutes. In other words, though the activity-coefficient is an exact expression of the mass-action of the ions, it shows nothing about their concentration or about the concentration of the unionized substance present with them. In most applications of the mass-action law it suffices to know the activities of the ions involved, a knowledge of the actual ionization being superfluous. In other applications where the concentration of the unionized substance must be evaluated, it is necessary to estimate the ionization. As there is no experimental basis for making this estimate, some supplementary hypothesis must be employed in these cases, for example, the hypothesis stated in Art. 79 that the ionization of largely ionized substances is complete.

*Applications of the Activity Principles and Comparison of the Results with Those Obtained by the Usual Methods. —*

*Prob. 58. — a.* Calculate the activity-coefficient of the OH ion-constituent, that is, the ratio of its activity to the activity or concentration of the  $\text{NH}_4\text{OH}$ , in a solution 0.1 f. in  $\text{NH}_4\text{OH}$  and 0.2 f. in  $\text{NH}_4\text{Cl}$  at  $25^\circ$ , assuming that the  $\text{NH}_4^+$  and  $\text{Cl}^-$  ions have equal activities in the solution, and taking  $1.8 \times 10^{-5}$  as the ionization-constant of  $\text{NH}_4\text{OH}$ . *b.* Calculate the ionization of the  $\text{NH}_4\text{OH}$  in the solution under the assumptions that the conductance-viscosity-ratio for  $\text{NH}_4\text{Cl}$  is equal to its ionization and that its ions are perfect solutes. *c.* Calculate the ionization of the  $\text{NH}_4\text{OH}$  under the assumptions that the  $\text{NH}_4\text{Cl}$  is completely ionized and that the ions are perfect solutes. *d.* Tabulate the results of these three calculations so as to show the different consequences of the activity principle and of the two simplifying assumptions.

*Prob. 59.*—When a 0.06 formal solution of  $\text{Cl}_2$  in water at  $0^\circ$  has come to equilibrium, it is found (by the method illustrated in Prob. 36 of Art. 80) that 31% of the  $\text{Cl}_2$  has undergone change according to the equation  $\text{Cl}_2 + \text{H}_2\text{O} = \text{H}^+\text{Cl}^- + \text{HOCl}$ . *a.* Calculate the equilibrium-constant of this reaction assuming that the HCl is completely ionized and that its ions are perfect solutes. *b.* Calculate under these assumptions the percentage of the  $\text{Cl}_2$  that would undergo change in a solution that is 0.06 formal in  $\text{Cl}_2$  and 0.2 formal in HCl at the beginning, first simplifying the equation by omitting negligible quantities. *c.* Calculate the equilibrium-constant using the true activity-coefficient for HCl obtained from the above table. *d.* Solve the problem stated in *b*, using true activity-coefficients. *e.* Tabulate the results of these four calculations, so as to show the differences resulting from the use of the approximate and exact methods of treatment.

*Prob. 60.*—The solubility of  $\text{TlCl}$  in water is 0.0161 formal at  $25^\circ$ . Calculate its solubility in a 0.05 formal KCl solution under the following assumptions: *a.* that the two salts are completely ionized and that their ions are perfect solutes; *b.* that the ionization of each salt is that given by the conductance-viscosity ratio for KCl at a concentration equal to the total salt concentration in the solution; *c.* that the activity-coefficient for each salt is equal to that for KCl at a concentration equal to the total salt concentration in the solution. *d.* Tabulate the results of these three calculations together with the experimentally determined solubility, which is 0.0059 formal. (The deviation of the value calculated with the activity-coefficients from the observed value is probably due to inaccuracy in the assumption that the activity-coefficient for  $\text{TlCl}$  is equal to that of KCl at the same concentration.

## CHAPTER VIII

### EQUILIBRIUM OF CHEMICAL SYSTEMS IN RELATION TO THE PHASES PRESENT

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#### I. GENERAL CONSIDERATIONS

**114. General Considerations.** — In this chapter are considered the principles relating to the number, state of aggregation, and composition of the phases (defined as in Art. 35) which coexist in equilibrium with one another when systems composed of one substance or of two or more substances in various proportions are subjected to different temperatures and pressures.

The kinds of phenomena to be considered are illustrated by the following examples. The state in which the substance water exists is determined by the temperature and pressure. Thus these conditions determine whether it exists in the form of a single phase as ice, as liquid water, or as vapor; in the form of two phases as ice and liquid water, as ice and vapor, or as liquid water and vapor; or in the form of the three phases, ice, liquid water, and vapor. So also in the case of two substances, such as carbon bisulfide and acetone, there are, as shown by the vapor-pressure-composition and boiling-point-composition diagrams of Arts. 42 and 43, definite conditions of pressure and temperature at which any definite mixture of the two substances forms two phases — a liquid phase and a vapor phase; and under these conditions the composition of each phase is also definite.

A *system* (Art. 23) is determined by its composition, that is, by the nature and quantities of its components; the *components* being any substances out of which the systems under consideration can be made up, through the use of the smallest possible number of such substances. The *state* of a system is definite when it has certain definite phases and when the specific properties of each phase, such as its density, specific conductance, index of refraction, etc., have definite values. In order that the specific properties of any one phase of a system may be fully determined, it is necessary to specify, in addition to the proportions of its components, any external factors which affect these properties. The only external factors which commonly have an appreciable influence are the pressure and temperature; and, in the following considerations relating to the equilibrium of phases, these factors

alone are taken into account, and their values are assumed to be uniform throughout all the phases of a system.

It is a fundamental law of the equilibrium between phases that the absolute quantity of the different phases does not influence their composition. Thus the composition of a solution in equilibrium with a solid salt is not dependent on the quantity of the solid in contact with the solution. The composition of the vapor in equilibrium with a definite liquid solution is not dependent on the quantities of liquid and vapor in contact with one another. The proportion of hydrogen and water-vapor in equilibrium with solid iron and solid ferrous oxide is not dependent on the quantities of these solid phases in contact with the gaseous phase. The *rate* at which equilibrium is established between phases is, however, greatly increased by increasing the extent of the surfaces between them.

The purpose of this chapter may now be more definitely stated. Its purpose is to show how the nature, the quantity, and the composition of the phases of a series of systems of the same qualitative composition vary when the composition of the system as a whole and the pressure and temperature are varied. One-component systems are first considered; then a general principle, known as the phase rule, applicable to systems with any number of components, is presented; and finally two-component and three-component systems are discussed.



and sulfur-vapor are in equilibrium with one another. A point, like this, at which three phases coexist is called a *triple point*.

The (vapor-pressure) curve CD represents the pressures at which liquid sulfur and sulfur-vapor are in equilibrium with each other at various temperatures; and the (melting-point) curve CF represents the temperatures at which monoclinic sulfur and liquid sulfur are in equilibrium at various pressures. The point C is evidently a second triple point at which monoclinic sulfur, liquid sulfur, and sulfur-vapor coexist. As indicated on the diagram, the fields between the different lines show the conditions under which sulfur exists as a single phase.

*Prob. 1. — Behavior of Sulfur Derived from the Diagram. —* Describe with the aid of the diagram the changes that take place, *a*, when sulfur is heated in an evacuated tube in contact with its vapor from  $90^{\circ}$  to  $125^{\circ}$ ; *b*, when sulfur is allowed to cool from  $125^{\circ}$  to  $90^{\circ}$ , the pressure being kept constant at 0.04 mm.

The curves BE and CF in the figure are very nearly vertical lines; for increase of pressure always produces a relatively small change in the transition or melting temperature. Thus the transition-temperature of the two solid forms of sulfur increases about  $0.04^{\circ}$ , and the melting-point of monoclinic sulfur increases about  $0.03^{\circ}$ , per atmosphere of pressure. With certain substances the effect of pressure is to decrease the transition or melting temperature; thus the melting-point of ice is lowered by  $0.0076^{\circ}$  by an increase of pressure of one atmosphere. The direction and magnitude of this effect can be derived from thermodynamic considerations, as shown in Art. 165.

*Unstable Forms. —*

*Prob. 2. — a.* To what equilibria do the curves BG, GC, and GH and the point G in the figure correspond? *b.* Considered with reference to these equilibria, to what form of sulfur do the fields EBGH, HGCF, and GBC correspond? *c.* In what sense are these equilibria unstable?

*Prob. 3. —* Draw a sulfur diagram extending to pressures above the triple-point for rhombic, monoclinic, and liquid sulfur, which lies at 151° and 1280 atm.

*Prob. 4. —* It will be noted that the unstable form at any temperature has the greater vapor-pressure. Prove that this must be so by showing what would happen if the two forms were placed beside each other in an evacuated apparatus.

*Prob. 5. —* Prove by a similar consideration that the unstable form must also have the greater solubility in any solvent, such as carbon bisulfide. (Note that a substance is commonly present in the same molecular form in the solutions produced by dissolving its different solid forms.)

How great the tendency is for a substance to remain in the same form after passing through a melting-temperature or transition-temperature and thus to exist in an unstable form depends in large measure on the nature of the substance. The following general statements in regard to it can, however, be made. A crystalline solid cannot as a rule be heated appreciably above its melting-point; thus, ice always melts sharply at  $0^{\circ}$  (under a pressure of 1 atm.). On the other hand, a liquid (like water) can ordinarily be cooled to a temperature considerably below the freezing-point if agitation and intimate contact with solid particles, especially with the stable solid phase, is avoided. Still more pronounced is the tendency of solid substances to remain in the same form upon being heated or cooled through a transition-temperature; thus rhombic sulfur can be heated to its melting-point ( $110^{\circ}$ ), although this is about  $15^{\circ}$  higher than the transition-temperature ( $95.5^{\circ}$ ) at which it should go over into monoclinic sulfur; and monoclinic sulfur can be cooled to room temperature without going over into the rhombic form, provided this be done quickly and without agitation.

The rate at which an unstable phase goes over into the stable one tends to increase with the distance from the transition-temperatures; but when the substance is below its transition-temperature this tendency may be more than compensated by the greatly reduced rate of reaction which a considerable lowering of temperature always produces; thus white phosphorus is an unstable form, but the rate at which it goes over into the stable red form at room temperature is so small that it may be preserved unchanged for years; similarly, diamond is an unstable form of carbon at room temperature, but it does not go over into graphite or amorphous carbon.

An effective means of causing an unstable form to go over into a stable one is to mix it intimately with the stable form. The transition may also be accelerated by moistening the mixture of the two forms with a solvent in which they are somewhat soluble. These facts are made use of in the determination of transition-temperatures. Thus the transition-temperature of sulfur has been determined by charging a bulb with a mixture of rhombic and monoclinic sulfur, filling it with carbon bisulfide and oil of turpentine, keeping it for an hour first at  $95^{\circ}$  and then at  $96^{\circ}$ , and noting whether the liquid rose or fell in the capillary stem attached to the bulb. The volume was found to decrease steadily at  $95^{\circ}$  (owing to the transition of the mono-

clinic into the rhombic form), and to increase steadily at  $96^{\circ}$  (owing to the reverse transition), showing that the transition-temperature lies between  $95$  and  $96^{\circ}$ .

*Prob. 6. — Transition in Relation to Solubility.* — *a.* Suggest an explanation of the catalytic action of the solvent in accelerating the transition of the sulfur. *b.* Outline a method by which the transition-temperature of sulfur could be determined by quantitative solubility measurements.

## III. THE PHASE RULE

**116. The Concept of Variance and Inductive Derivation of the Phase Rule.** — There will next be considered a principle, called the phase rule, which serves as a basis of classification of different types of equilibrium and enables the number of phases that exist under specified conditions to be predicted. There must, however, first be presented a concept involved in that principle — that of variance.

*Prob. 7. — Number of Factors Determining the State of One-Component Systems.* — Assuming that sulfur is kept at a specified pressure of 0.04 mm., state at what temperatures it is stable, *a*, in a single phase as rhombic sulfur, as monoclinic sulfur, and as liquid sulfur; *b*, in two phases, as rhombic and monoclinic sulfur, and as monoclinic and liquid sulfur; *c*, in the three phases, rhombic sulfur, monoclinic sulfur, and sulfur-vapor.

It will be noted that, in order to determine the position on the diagram and therefore the state of the system, the values of two determining factors, namely, the values of both the pressure and the temperature, must be specified when there is only one phase; that the value of only one of these factors, either the temperature or pressure, need be specified when any two phases coexist; and that no condition can be arbitrarily specified when any three phases coexist.

The number of determining factors whose values can and must be specified in order to determine the state of a system consisting of definite phases and components is called its *variance* or number of degrees of freedom; and, corresponding to the number of such factors, systems are said to be *nonvariant*, *univariant*, *bivariant*, etc.

It is evident from the preceding statements that when a one-component system consists of only one phase the system is bivariant, when it consists of two phases it is univariant, and when it consists of three phases it is nonvariant. In other words, the sum of the variance and number of phases is always three for a one-component system.

*Relation of Variance to Number of Phases. —*

*Prob. 8.* — Discuss with reference to the principle just stated and to the sulfur diagram the possibility of the coexistence, *a*, of the three phases, rhombic, monoclinic, and liquid sulfur; *b*, of the four phases, rhombic, monoclinic, liquid, and gaseous sulfur.

*Prob. 9.* — Consider the following systems existing in the phases indicated:

- (1) Solution of  $\text{C}_2\text{H}_5\text{OH}$  and  $\text{H}_2\text{O}$ .
  - (2) Two solutions,  $\text{Br}_2$  in  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}$  in  $\text{Br}_2$ .
  - (3) Two solutions,  $\text{Br}_2$  in  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}$  in  $\text{Br}_2$ ; and their vapors.
  - (4) Two solutions,  $\text{Br}_2$  in  $\text{H}_2\text{O}$ , and  $\text{H}_2\text{O}$  in  $\text{Br}_2$ ; their vapors; ice.
  - (5) Solution of  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and  $\text{HC}_2\text{H}_3\text{O}_2$ .
  - (6) Solution of  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , and  $\text{HC}_2\text{H}_3\text{O}_2$ ; and their vapors.
- a.* Upon the basis of the principles already considered relating to solubility, vapor-pressure, and freezing-point, name definitely certain factors the specification of whose values will fully determine all the properties of each of these systems. *b.* Make a table showing the number of components, the number of phases, the variance, and the sum of the number of phases and the variance, for each of these systems. Note that the specific properties of any one phase, such as its density, specific heat-capacity, or refractive index, have definite values only when it is at some definite temperature and pressure and when it has a definite composition, which may be determined by specifying the mol-fractions of all but one of its components.

These problems show that in every case the sum of the number of phases ( $P$ ) and of the variance ( $V$ ) is greater by two than the number of the components ( $C$ ); that is,  $P + V = C + 2$ . This principle, which is called the *phase rule*, is a general one, applicable to systems consisting of any number of components and of any number of phases.

The phase rule furnishes a basis for the classification of different types of equilibrium. It also enables the number of phases that can exist under specified conditions to be predicted. The usefulness of the phase rule itself is, however, often exaggerated. Of primary importance in the treatment of the equilibrium conditions of systems in relation to the phases present are the methods of representing those conditions by diagrams, as described in later articles of this chapter.

*Prob. 10. — Number of Phases Permitted by the Phase Rule.* — Sodium carbonate and water form solid phases of the composition  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$ , and  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ . *a.* State how many of these hydrates could exist in equilibrium with the solution and ice under a pressure of 1 atm. *b.* State how many of these hydrates could exist in equilibrium with water-vapor at  $30^\circ$ .

**\*117. Discussion of the Concept of Components.** — The substances to be regarded as the components, and correspondingly the number of components, are obvious in cases, like those already considered, in which there is no transformation of the components into other chemical substances. In cases where a chemical action occurs, the term component requires to be more specifically defined, which may be done

as follows. It is evident from the preceding derivation of the phase rule (and from that in Art. 118) that in general any substances may be selected as the *components*, the specification of the relative quantities of which in any phase suffices to determine fully the composition of that phase; the components, moreover, being such that this is true whatever phase of the system is considered. This definition is illustrated by the following examples.

The composition of a gaseous phase containing hydrogen, oxygen, and water-vapor in equilibrium with one another at any definite temperature and pressure is fully determined by specifying the relative quantities of total hydrogen and total oxygen present, either as the elementary substances or as constituents of the water; for then the proportions of the three substances adjust themselves so as to satisfy the conditions of the equilibrium between them, for example, so as to satisfy the mass-action law if the substances are perfect gases. The number of components in this case is therefore two.

The composition of a gaseous phase containing hydrogen, oxygen, and water-vapor at low temperatures where there is no reaction between the substances is evidently determined only when the relative quantities of hydrogen, oxygen, and water in the phase are specified. The number of components is therefore three under these conditions.

It is obvious from these examples that the number of components is determined not only by the substances present, but also by the equilibria that are established between them. It is therefore advisable to write chemical equations expressing all the equilibria actually established, so as to make sure that the proportion of every chemical substance present in any phase would be determined by specifying that definite relative quantities of the components adopted are present in that phase, and to make sure, on the other hand, that more components have not been adopted than are necessary.

Another aspect of the matter may be considered. In a gaseous phase where hydrogen, oxygen, and water are in chemical equilibrium, one particular system could be produced by taking water as the only component; but the phase considerations of this chapter have reference always to a series of systems of the same qualitative, but varying quantitative composition; and such a series containing hydrogen, oxygen, and water-vapor in every possible proportion cannot be produced out of water alone, but can be produced out of hydrogen and oxygen. These systems are therefore properly regarded as consisting

of two components. As another example consider a gaseous phase containing HCl, O<sub>2</sub>, Cl<sub>2</sub>, and H<sub>2</sub>O. By taking HCl and O<sub>2</sub> as two components, the other two substances can be produced out of them by the reaction  $O_2 + 4HCl = 2Cl_2 + 2H_2O$ , but only in equivalent proportions. To produce a system containing the four substances in any proportion whatsoever, it is necessary to make use of a third component, either Cl<sub>2</sub> or H<sub>2</sub>O. Thus, either by adding Cl<sub>2</sub> to a mixture containing O<sub>2</sub> and HCl in any proportions and Cl<sub>2</sub> and H<sub>2</sub>O in equivalent proportions, or by removing Cl<sub>2</sub> from such a mixture, any composition whatever can be secured. The systems are therefore said to consist of three components. It may be further noted that, though the number of components is fixed, there is a certain arbitrariness in their selection. Thus, although in this example O<sub>2</sub>, HCl, and Cl<sub>2</sub> have been used as the components, any other three of the four substances might be employed. It is, however, usual to select as components the simplest substances.

*Determination of Components.—*

*Prob. 11.* — Specify the components which will produce phases containing the following chemical substances, assuming chemical equilibrium to be established between them. In answering this question, write chemical equations expressing all the equilibria that may be established between these substances, making sure that all the substances can be produced in any proportion from the specified components, and that all those components are necessary. *a.* Gaseous H<sub>2</sub>, O<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O. *b.* Solution containing H<sub>2</sub>O, (H<sub>2</sub>O)<sub>2</sub>, NaCl.2H<sub>2</sub>O, NaCl, Na<sup>+</sup>, Cl<sup>-</sup>. *c.* Solution containing H<sub>2</sub>O, NH<sub>4</sub>CN, NH<sub>4</sub><sup>+</sup>, CN<sup>-</sup>, NH<sub>3</sub>, NH<sub>4</sub>OH, HCN.

*Prob. 12.* — Specify the components of the systems that exist in the following groups of phases, assuming chemical equilibrium to be established between the substances named: *a.* Solid NH<sub>4</sub>Cl, gaseous NH<sub>3</sub> and HCl. *b.* Solid CaCO<sub>3</sub>, solid CaO, gaseous CO<sub>2</sub>. *c.* Solid MgSO<sub>4</sub>.7H<sub>2</sub>O, solid MgSO<sub>4</sub>.6H<sub>2</sub>O, solution of Mg<sup>++</sup>SO<sub>4</sub><sup>=</sup> in water, water-vapor. *d.* Solid carbon; gaseous H<sub>2</sub>O, H<sub>2</sub>, CO, and CO<sub>2</sub>. *e.* Solid iron, solid FeO, gaseous CO and CO<sub>2</sub>. *f.* Solid iron, solid FeO, solid carbon, gaseous CO and CO<sub>2</sub>.

**\*118. Derivation of the Phase Rule from the Perpetual-Motion Principle.** — In order to determine fully the state of one-phase systems consisting of any number *C* of components (as defined in Art. 117), evidently the composition of the phase and in addition any external factors that determine its properties must be specified. The composition of the phase is fully determined by specifying the mol-fractions of all but one of the components, that is, by specifying *C* — 1 quanti-

ties. The only external factors which commonly affect the properties of a phase of specified composition are temperature and pressure; but in special cases certain other factors, some of which are mentioned below, have an appreciable influence. Representing the number of such external determining factors by  $n$ , the variance or total number of the independent variables that must be specified is  $C - 1 + n$ . In any system, therefore, in which the number of phases  $P$  is one, the sum of the number of phases and the variance  $V$  is equal to  $C + n$ ; that is,  $P + V = C + n$ ; or, for the common case where pressure and temperature are the only external determining factors,  $P + V = C + 2$ . For example, the state of one-phase systems consisting of three components (1, 2, 3) is fully determined by specifying four quantities, namely, the mol-fractions ( $x_1$  and  $x_2$ ) of any two of the components and the pressure ( $p$ ) and temperature ( $T$ ); hence any specific property whatever of the system, such as its density  $d$ , can be expressed as some function of these four variables, such as  $d = f(x_1, x_2, p, T)$ . In the general case, where the number of components is  $C$  and the number of external factors is  $n$ , the function becomes

$$d = f(x_1, x_2, \dots, x_{C-1}, p, T, \dots).$$

The derivation of the phase-rule now consists in showing that the equation  $P + V = C + n$ , which for one-phase systems is a result of the definitions of components and of external factors, still holds true whatever be the number of phases. In order that this may be so, it is evidently necessary only that each new phase introduced into the system shall diminish the variance by one; for then  $P + V$  will still have its former value  $C + n$ . That this is the case can be shown as follows.

Consider that a system of  $C$  components (1, 2, 3, . . .  $C$ ) exists as a gaseous phase, and that a new liquid or solid phase is developed in it (for example, by varying the pressure or temperature). Now the partial pressures ( $p_1, p_2, \dots, p_C$ ) of the separate components in the gaseous phase are, like any other property of the phase, functions only of the mol-fractions ( $x_1, x_2, \dots, x_{C-1}$ ) and of the external factors ( $p, T, \dots$ ). This conclusion may be expressed mathematically as follows:

$$p_1 = f_1(x_1, x_2, \dots, x_{C-1}, p, T, \dots).$$

$$p_2 = f_2(x_1, x_2, \dots, x_{C-1}, p, T, \dots).$$

$$\dots\dots\dots$$

$$p_C = f_C(x_1, x_2, \dots, x_{C-1}, p, T, \dots).$$

When the new, liquid or solid, phase is present in equilibrium with the gaseous phase, the partial pressure of each component in the gaseous phase is determined by the mol-fractions ( $x_1', x_2', \dots x'_{c-1}$ ) of the liquid or solid phase, by the temperature, and by any other external determining factor which has an appreciable influence; for, if a liquid or solid phase of such composition as to be in equilibrium with the gaseous phase could also be in equilibrium at the same temperature with some other gaseous phase with different partial pressures, perpetual motion of the kind described in Art. 44 could be realized. This conclusion from the perpetual-motion principle that the partial pressures must be fully determined by the mol-fractions in the liquid phase and by the external factors may be expressed mathematically as follows:

$$p_1 = f_1'(x_1', x_2', \dots x'_{c-1}, p, T, \dots).$$

$$p_2 = f_2'(x_1', x_2', \dots x'_{c-1}, p, T, \dots).$$

$$\dots\dots\dots$$

$$p_c = f_c'(x_1', x_2', \dots x'_{c-1}, p, T, \dots).$$

By equating these two sets of expressions for  $p_1, p_2, \dots p_c$ , the following functional relations between the mol-fractions in the gaseous phase and those in the liquid phase are obtained:

$$f_1(x_1, x_2, \dots x_{c-1}, p, T, \dots) = f_1'(x_1', x_2', \dots x'_{c-1}, p, T, \dots).$$

$$f_2(x_1, x_2, \dots x_{c-1}, p, T, \dots) = f_2'(x_1', x_2', \dots x'_{c-1}, p, T, \dots).$$

$$\dots\dots\dots$$

$$f_c(x_1, x_2, \dots x_{c-1}, p, T, \dots) = f_c'(x_1', x_2', \dots x'_{c-1}, p, T, \dots).$$

That is, the new phase gives us  $C$  new functional equations in which only  $C - 1$  new variables (namely,  $x_1', x_2', \dots x'_{c-1}$ ) are introduced. By combining these new equations with one another the new variables may evidently be eliminated, yielding a functional relation of the form:

$$f_1(x_1, x_2, \dots x_{c-1}, p, T, \dots) = 0.$$

This is obviously a relation between the  $C - 1 + n$  variables which determine any property of the gaseous phase, in the way described in the first paragraph of this article. Hence the number of these variables whose values can and must be specified to determine the properties of the gaseous phase is one less than it was when that phase was alone present. And in a similar way this can be shown to be true also of the properties of the liquid or solid phase. In other words, the new phase diminishes the variance of the system by one, and the sum  $P + V$  retains the value  $C + n$  which it had when the system consisted

of a single phase. And evidently, since each additional phase formed within the system will similarly decrease the variance by one, the sum  $P+V$  will always have the same value  $C+n$ .

In the above derivation it was assumed that a gaseous phase was present in the system. It will be noted, however, that the partial pressures in the gaseous phase were employed only as a means of deriving functional relations between the mol-fractions of the components in two different phases, and that the partial pressures disappeared in these relations. This indicates, and it can be rigorously shown, that functional relations between the mol-fractions of the same form as those given above hold true for any pair of phases; for example, for two liquid phases. It follows, therefore, that the phase rule is applicable to any kind of system whatever, in the form  $P+V=C+n$ .

As has been stated, the value of  $n$  in the above derived expression of the phase rule is commonly 2; for the only external factors that ordinarily influence appreciably the state of the system are temperature and pressure. In some cases, however, other factors come into play. For example, this is sometimes true of intensity of illumination or of electric or magnetic field. Thus illumination of silver chloride increases its dissociation-pressure; and under certain conditions an electric discharge through an equilibrium mixture of nitric oxide, nitrogen, and oxygen increases the proportion of nitric oxide in the mixture. Another factor which makes the value of  $n$  greater than 2 is introduced when different pressures are applied by means of semi-permeable walls to different phases of the system. Thus the pressure of the vapor in equilibrium with a liquid is progressively increased (as shown in Art. 51) when the liquid is subjected to an increasing pressure by means of a piston permeable for the vapor only. A common case of this kind is that where the atmosphere acts as such a piston, exerting a pressure on the liquid and solid phases of the system, but not on the components in the vapor phase.

## IV. TWO-COMPONENT SYSTEMS

**119. Systems with Solid and Gaseous Phases.** — The equilibrium of systems consisting of solid and gaseous phases at constant temperature has already been considered from the mass-action viewpoint in Art. 110. Their equilibrium in relation to temperature and pressure will now be considered from the phase-rule viewpoint.

When a two-component system consists of three phases, the phase rule evidently shows that the specification of one of the determining factors (for example, the temperature) fixes the state of the system and therefore the values of the other factors (for example, of the pressure and of the composition of the liquid or the gaseous phase). The pressures at which the different groups of three phases exist in equilibrium at various temperatures can therefore be represented by lines on a diagram in which the pressure and temperature are the coördinates.

*Dissociation-Pressure and its Relation to Temperature. —*

**Prob. 13.** — Calcium carbonate dissociates at high temperatures into CaO and CO<sub>2</sub>. *a.* Show from the phase rule that CaCO<sub>3</sub> can be heated in CO<sub>2</sub> gas at a given pressure through a certain range of temperature without any decomposition taking place. *b.* Show also that there is one temperature, and only one, at which a mixture of CaCO<sub>3</sub> and CaO can be kept under CO<sub>2</sub> at the given pressure without any change occurring.

**Prob. 14.** — The dissociation-pressure of solid calcium carbonate

is	10	180	320	580	760	1000 mm.
at	600°	800°	840°	880°	896°	910°

*a.* Construct a pressure-temperature diagram for this two-component system, lettering the fields so as to show what phases coexist at different temperatures and pressures. *b.* State at what temperature the solid begins to dissociate when it is heated in air free from carbon dioxide. *c.* State at what temperature it would dissociate completely when heated in a covered crucible (so that there is equalization of the pressure, but no circulation of air into the crucible). *d.* In lime-burning state what temperature would have to be maintained in the kiln if there were no circulation of gases through it. *e.* State what temperature would have to be maintained if the coal used as fuel were burned to carbon dioxide with the minimum quantity of air and the combustion-products were passed up through the kiln.

**Prob. 15.** — The dissociation pressure of silver oxide is 0.1 atm. at 116°, 0.2 atm. at 132°, 1.0 atm. at 175°, and 2.0 atm. at 197°. *a.* If finely divided silver be heated in the air, what proportion of it will be finally converted into oxide when the temperature is 130°? when it is 140°? *b.* How could silver oxide be heated to 170° without any decomposition?

**Prob. 16.** — Describe a method by which pure oxygen can be prepared from the air with the aid of the reaction  $2\text{BaO}_2(\text{s}) = 2\text{BaO}(\text{s}) + \text{O}_2(\text{g})$ .

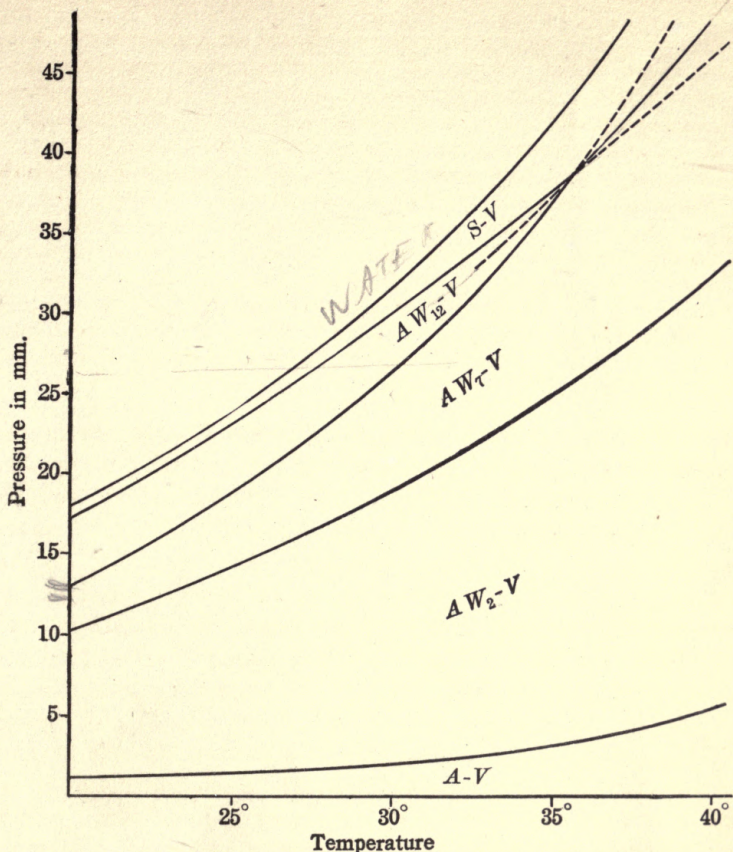
*Prob. 17.*—When a precipitate of hydrated manganese dioxide is ignited in the air it comes to a constant weight corresponding to the composition  $\text{MnO}_2$  when the temperature is  $450^\circ$ , and to another constant weight corresponding to the composition  $\text{Mn}_2\text{O}_3$  when the temperature is  $500^\circ$ ; but when ignited in oxygen it changes to  $\text{MnO}_2$  even at  $500^\circ$ . State what these facts show as to the dissociation-pressure of  $\text{MnO}_2$  into  $\text{Mn}_2\text{O}_3$ , and that of  $\text{Mn}_2\text{O}_3$  into a lower oxide.

*Prob. 18.*—A method has been suggested for the standardization of sulfuric acid solutions which consists in adding an excess of ammonia solution, evaporating, drying the residue at  $100^\circ$ , and weighing it. In drying the salt some decomposition according to the reaction  $(\text{NH}_4)_2\text{SO}_4(\text{s}) = \text{NH}_4\text{HSO}_4(\text{s}) + \text{NH}_3(\text{g})$  is likely to take place. How might the process be modified so as to hasten the drying and yet entirely prevent the decomposition?

**120. Systems with Solid, Liquid, and Gaseous Phases. Pressure-Temperature Diagrams.**—The two-component systems that involve salt-hydrates are of especial importance. The vapor-pressure relations of these substances at different temperatures may be represented by pressure-temperature diagrams, like that shown on the next page. This diagram has reference to systems consisting of the two components disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) and water ( $\text{H}_2\text{O}$ ), for the case that the vapor-phase (V), which consists only of water-vapor, is always present. These two components form the following solid phases: ice (I), anhydrous salt (A), dihydrate  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$  ( $\text{AW}_2$ ), heptahydrate  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$  ( $\text{AW}_7$ ), and dodecahydrate  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  ( $\text{AW}_{12}$ ); also a solution-phase (S) of variable composition, approaching as one limit pure water, whose vapor-pressure is represented by the uppermost curve in the diagram.

The phase rule evidently requires that in systems of this kind, in addition to the vapor-phase, two solid phases, or one solid and one liquid phase, must be present in order that the pressure of the vapor may have a definite value at any definite temperature.

*Prob. 19.*—*Interpretation of the Vapor-Pressure-Temperature Diagram for Salt-Hydrates.*—At  $30^\circ$  one formula-weight of  $\text{Na}_2\text{HPO}_4$  is placed in contact with a large volume of water-vapor at 1 mm., and the volume of the vapor is steadily diminished (so slowly that equilibrium is established) until finally there remains in contact with the vapor only the saturated solution (which contains the components in the ratio  $1\text{Na}_2\text{HPO}_4 : 33.2\text{H}_2\text{O}$ ). State, with the aid of the figure, the changes that take place in the pressure of the vapor and the accompanying changes that take place in the character of the other phases in contact with it, throughout the whole process.



*Prob. 20. — Vapor-Pressure-Composition Diagram for Salt-Hydrates. — a.* Plot the pressure of the vapor (as ordinates) against the number of formula-weights of water absorbed by the salt as abscissas for the process described in Prob. 19 (up to the point where 15 formula-weights have been absorbed). Mark the lines on the plot so as to show what phases are present during each stage of the process. *b.* Make a similar plot for the case that the process described in Prob. 19 takes place at 38° (instead of at 30°).

*Prob. 21. — Experimental Determination of the Hydrates Formed by a Salt. —* Describe an experimental method of determining what hydrates of copper sulfate exist at 25°.

*Prob. 22. — Transition-Temperature of Salt-Hydrates. —* Describe with the aid of the figure what changes take place when a mixture of heptahydrate and dodecahydrate is heated from 30° to 38° in a sealed tube previously evacuated.

*Prob. 23. — Conditions under which Salts are Efflorescent or Hygroscopic.* — At  $30^\circ$  moist air is in contact with solid  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ . Under what conditions of humidity, *a*, would the salt remain unchanged? *b*, would it lose water? *c*, would it absorb water? (By the *humidity* of a gas is meant the ratio of the pressure of the water-vapor in the gas to the vapor-pressure of water at the same temperature.)

*Prob. 24. — Drying of Hydrates without Decomposition.* — *a*. State the conditions under which moist crystals of  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  could be completely dried at  $30^\circ$  without danger of decomposition. *b*. Describe a method by which these conditions could be practically realized.

*Separation of Hydrates from Solutions.* —

*Prob. 25.* — State what solid phase separates on evaporating a dilute solution of  $\text{Na}_2\text{HPO}_4$ , *a*, at  $30^\circ$ , *b*, at  $38^\circ$ .

*Prob. 26.* — The equilibrium-pressures for the reaction  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (gypsum) =  $\text{CaSO}_4$ (anhydrite) +  $2\text{H}_2\text{O}(\text{g})$  and the vapor-pressures of pure water at various temperatures are as follows:

Temperature . . .	$50^\circ$	$55^\circ$	$60^\circ$	$65^\circ$
Gypsum . . . .	80	109	149	204 mm.
Water . . . . .	92	118	149	188 mm.

The solubility of calcium sulfate is so small that the vapor-pressure of its saturated solution may be considered to be identical with that of water. *a*. State what happens on heating gypsum from  $50^\circ$  to  $65^\circ$  in a sealed tube previously evacuated. *b*. State what solid phase separates when a solution of calcium sulfate is evaporated at  $55^\circ$ , and at  $65^\circ$ . *c*. State what solid phase would separate upon evaporating the solution at  $55^\circ$  if, when it became saturated, enough calcium chloride were added to reduce its vapor-pressure by 10%. Give the reasons in each case.

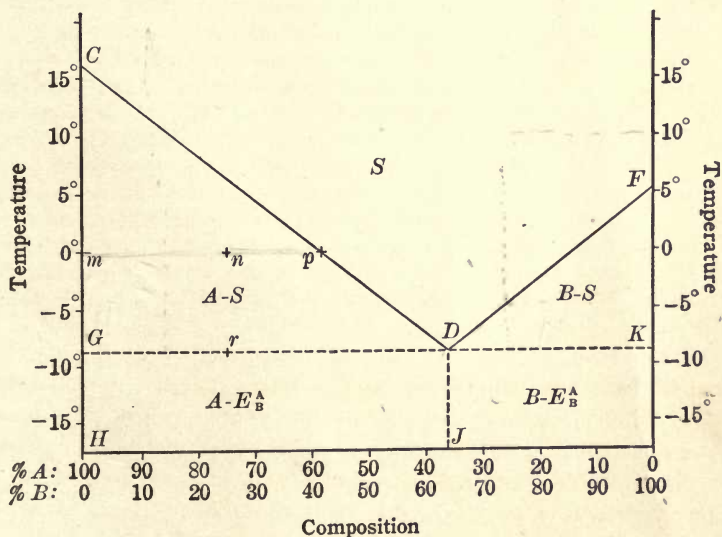
*Prob. 27. — Dehydration of Organic Liquids by Salts.* — Determine the extent to which the mol-percent of water in isoamyl alcohol can be reduced by shaking at  $25^\circ$  isoamyl alcohol saturated with water with a large excess of each of the following substances: *a*,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ; *b*,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ ; *c*,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ ; *d*,  $\text{Na}_2\text{HPO}_4$ . For the data refer to the diagrams of this article and of Prob. 47, Art. 47.

**121. Systems with Solid and Liquid Phases. Temperature-Composition Diagrams.** — In a two-component system the composition of a solution which coexists with its vapor and a solid phase is evidently fully determined by specification of the temperature, the system being univariant. The relation between this composition and the temperature can therefore be represented by a diagram in which these factors are plotted as coördinates.

It is evident that the equilibrium conditions of a two-component system can still be represented by a temperature-composition diagram when the specification that the vapor-phase is present is replaced by

the specification that the pressure has some definite value (greater than that at which the vapor can exist). Moreover, since pressure has, as illustrated in Art. 115, only a small effect on equilibria in which solid and liquid phases are alone involved, the lines on the temperature-composition diagram have substantially the same position when the system is under a pressure of one atmosphere as they do when it is under the pressure of the vapor. And in practice composition-temperature diagrams are ordinarily constructed from data determined under the atmospheric pressure.

The form of the temperature-composition diagram varies greatly with the character of the solid phases which the components are capable of producing. The simplest type of such a diagram is that in which the two components A and B do not form any solid compound with each other, but separate from the solution in the pure state. This type is illustrated by the figure, which shows the complete diagram for systems composed of acetic acid (A) and benzene (B) at one atmosphere.



The freezing-point curve CD represents the composition of the solutions (S) which are in equilibrium with solid A, and the freezing-point curve DF represents the composition of the solutions which are in equilibrium with solid B at different temperatures. The point D at

which the solution is in equilibrium with the two solid phases A and B is called the *eutectic point*. When a solution in the condition corresponding to this point is cooled, it solidifies completely without change of composition or temperature to a mixture of the two solid phases A and B. This mixture is usually so fine-grained and intimate that it differs markedly in texture from ordinary mixtures of the same solid phases. It is called the *eutectic mixture*, or simply the *eutectic*.

*Prob. 28. — Eutectics in Relation to the Phase Rule.* — Show that the phase rule requires that a solution at the eutectic point solidify without change of temperature or composition when heat is withdrawn from it.

*Prob. 29. — Effect of Cooling a Solution Predicted from the Diagram.* — A tube containing a solution of 75% of benzene and 25% of acetic acid at  $10^{\circ}$  is placed within an air jacket surrounded by a freezing mixture at  $-20^{\circ}$ , so that the system slowly loses heat, till its temperature falls to  $-10^{\circ}$ . Predict with the aid of the figure the values of the temperature and composition of the solution at which any phase appears or disappears. State also the character of the solid mixture finally obtained.

*Prob. 30. — Cooling Curves.* — *a.* On a diagram having as ordinates the temperatures in degrees and as abscissas the time of cooling in arbitrary units draw curves representing in a general way the rate at which the temperature decreases when a solution of 75% of benzene and 25% acetic acid is cooled as described in Prob. 29, assuming, first, that the liquid overcools without the separation of any solid phase; and assuming, secondly, that the solid phases separate so that there is always equilibrium. Take into account the fact that on cooling a system there is always an evolution of heat whenever a new phase separates. *b.* Draw on the same diagram, at the right of these curves, a new cooling curve showing how the temperature changes when pure benzene is cooled from  $10^{\circ}$  to  $-10^{\circ}$ . *c.* Draw a cooling curve also for the case that a solution of 64% of benzene and 36% of acetic acid is cooled from  $10^{\circ}$  to  $-10^{\circ}$ .

The fields in the diagram also become of much significance, when the composition represented by the abscissas is understood to be that of the whole system — not merely that of the liquid phase. Thus, when the system consists of the substances in such a proportion (thus, 25% of B to 75% of A) and is at such a temperature (thus,  $0^{\circ}$ ) that its condition is represented by a point *n* within the field CDG, the diagram shows that it consists of the two phases, solid A and solution S of the composition (corresponding to the point *p*) at which these two phases are in equilibrium at the given temperature. Similarly, when the system has a composition and temperature corresponding to any point within the field GDJH, it consists of solid A and the eutectic mixture  $E_B^A$ .

which always has the composition corresponding to the point D. It can readily be shown, moreover, that, when the state of the system is represented by the point  $n$ , the weight of the solid A is to the weight of the solution present as the length of the line joining  $n$  and  $p$  is to the length of the line joining  $m$  and  $n$ ; and similarly, that at any point below  $r$  on the same ordinate with it the weight of pure A is to the weight of the eutectic mixture present as the length of the line  $rD$  is to that of the line  $Gr$ .

*Prob. 31. — Nature of the Solid Phases.* — How do the two rectangular fields at the bottom of the figure differ with respect to,  $a$ , the phases present;  $b$ , the texture of the mixture?

*Prob. 32. — Relative Weights of the Separate Phases.* — Show that the relation stated in the last sentence of the preceding text is true.

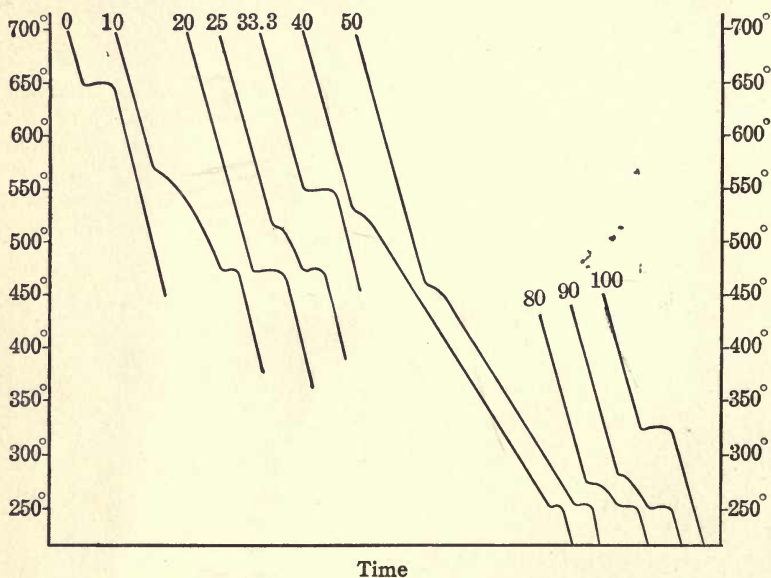
*Prob. 33. — Eutectic Composition and Temperature in Relation to the Laws of Freezing-Point Lowering.* — Lead (which melts at  $327^\circ$ ) and silver (which melts at  $960^\circ$ ) form a eutectic which melts at  $304^\circ$ . The heat absorbed by the fusion of one atomic weight of lead is 1340 cal. Calculate the composition of the eutectic, taking into account the facts that the first part of a freezing-point curve can be located with the aid of the laws of perfect solutions, and that the molecules of metallic elements in dilute metallic solutions are as a rule identical with their atoms. Compare the calculated composition of the eutectic with that (4.7 Ag to 95.3 Pb) derived from cooling curves.

*Prob. 34. — Metallurgical Process of Enriching Lead-Silver Alloys Resulting from the Reduction of Ores.* — A technical process of enriching lead-silver alloys has been based on the facts stated in Prob. 33. Describe how this process might be applied to a melt containing 1 at. wt. of silver and 99 at. wts. of lead, and state the extent to which the percentage of silver could be thereby increased.

The types of temperature-composition diagrams to be next considered are those for systems of which the components form one or more compounds which separate as solid phases. The simplest case, illustrated by Prob. 35, is that in which the solid compounds melt on heating. Another important case, illustrated by Prob. 36, is that in which a solid compound separates which, when heated, instead of melting, undergoes transition into another solid compound and a liquid phase.

The diagrams for such systems may be constructed either from cooling curves or from the results of solubility and freezing-point measurements. The former method is used in the case of alloys and other high-melting systems (as in Prob. 35); the latter, in the case of systems involving solutions at moderate temperatures (as in Prob. 36).

*Prob. 35. — Construction of Temperature-Composition Diagrams from Cooling Curves.* — The figure shows the cooling curves for a series of mixtures of magnesium and lead containing the atomic percentages of lead shown by the numbers at the tops of the curves. On a diagram whose coördinates are temperature and atomic percentages plot points representing the temperature at which the solidification of each mixture begins and ends. Draw in solid lines representing the freezing-point curves. Draw also dotted lines limiting the different fields (as was done in the benzene-acetic-acid diagram), and letter the fields so as to show of what the system consists in each field.



*Construction of a Temperature-Composition Diagram for Salt Hydrates.*

*Prob. 36.* — Construct a temperature-composition diagram for the system composed of  $\text{Na}_2\text{HPO}_4$  and  $\text{H}_2\text{O}$  by plotting the following values of the percentage (100  $x$ ) of  $\text{Na}_2\text{HPO}_4$  in the saturated solution as abscissas against the temperature ( $t$ ) as ordinates. The solid phase which is in equilibrium with the solution (S) at a pressure of 1 atm. is indicated by the letters above the data.

	<i>Ice</i>	<i>AW<sub>12</sub></i>	<i>AW<sub>12</sub></i>	<i>AW<sub>12</sub></i>	<i>AW<sub>12</sub></i>	<i>AW<sub>7</sub></i>
100 $x$	1.1	2.4	5.5	19.2	30.0	33.7
Temp.	—0.5°	0°	15°	30°	35°	38°
	<i>AW<sub>7</sub></i>	<i>AW<sub>7</sub></i>	<i>AW<sub>2</sub></i>	<i>AW<sub>2</sub></i>	<i>AW<sub>2</sub></i>	
100 $x$	38.0	43.5	44.7	46.6	48.0	
Temp.	43°	48°	50°	55°	60°	

Draw in on the diagram lines representing the equilibrium conditions, and mark each line with letters indicating the phases which coexist under the conditions represented by the line; and at each triple point designate the phases that coexist there, the temperature, and the composition of the solution.

*Prob. 37.*—As a means of determining what the fields in the diagram signify with respect to the phases present, proceed as follows.

*a.* State the solid phases that separate, and the way in which the composition of the residual solution changes, on cooling from  $55^{\circ}$  to  $-5^{\circ}$  at 1 atm. solutions containing 1% and 20% of  $\text{Na}_2\text{HPO}_4$ . Draw in on the diagram lines bounding the fields within which the phases ice I and solution S coexist, within which  $\text{AW}_{12}$  and solution coexist, and within which ice and  $\text{AW}_{12}$  coexist; and letter the fields correspondingly. (Note that at any definite temperature the composition limits of any such field are the compositions of the two phases that are in equilibrium at that temperature, since these are the limiting compositions of mixtures that can be made up of these two phases.) *b.* From a similar consideration deduce and state the results of cooling from  $55^{\circ}$  to  $-5^{\circ}$  solutions containing 36% and 42% of  $\text{Na}_2\text{HPO}_4$ . Draw in on the diagram lines bounding the fields within which the phases  $\text{AW}_7$  and solution S coexist, and within which the phases  $\text{AW}_{12}$  and  $\text{AW}_7$  coexist. (Note that, when the triple point is reached, the phase  $\text{AW}_{12}$  separates, thereby tending to decrease further the percentage of  $\text{Na}_2\text{HPO}_4$  in the solution; but, since the composition must remain constant so long as three phases are present, the phase  $\text{AW}_7$  re-dissolves; and this process continues as heat is withdrawn either till the phase  $\text{AW}_7$  is consumed or till the solution dries up.) *c.* Finally state the results of cooling from  $55^{\circ}$  to  $-5^{\circ}$  a solution containing 46% of  $\text{Na}_2\text{HPO}_4$ . Draw in on the diagram lines bounding the fields within which the phases  $\text{AW}_2$  and solution S coexist, and within which the phases  $\text{AW}_7$  and  $\text{AW}_2$  coexist.

*Prob. 38.*—*Preparation of Different Hydrates by Evaporation at Different Temperatures.*—Determine from the diagram within what limits of temperature a solution of  $\text{Na}_2\text{HPO}_4$  must be evaporated in order to obtain in the pure state, *a*,  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ; *b*,  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}$ ; *c*,  $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ . (The conditions under which such salt-hydrates can be dried without change in composition were considered in Prob. 24).

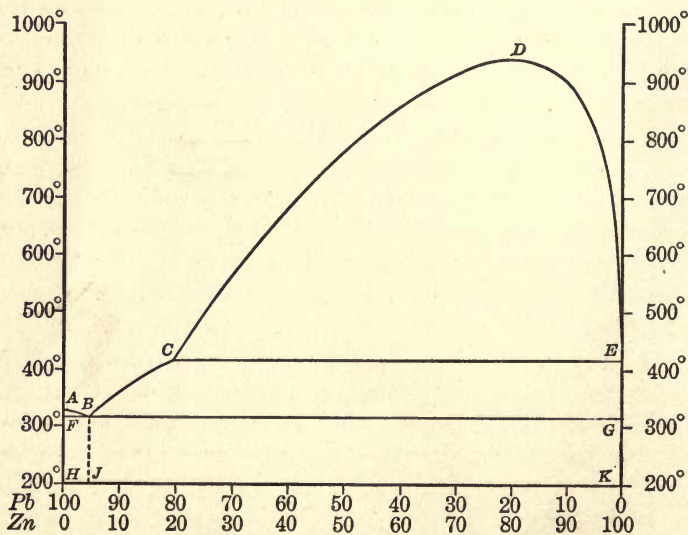
*Conditions of Unstable Equilibrium.*—

*Prob. 39.*—*a.* By extending by dotted lines the appropriate curves on the diagram, determine the solubilities, in terms of the percentage of anhydrous salt in the solution, of  $\text{AW}_7$  at  $45^{\circ}$  and  $50^{\circ}$ , and of  $\text{AW}_2$  at  $45^{\circ}$  and  $50^{\circ}$ . *b.* Prove that in contact with the solution  $\text{AW}_7$  is unstable at  $50^{\circ}$  with respect to  $\text{AW}_2$  by showing with the aid of these solubility values what happens when  $\text{AW}_7$  is placed in contact with a solution saturated at  $50^{\circ}$  with respect to  $\text{AW}_2$ . *c.* Show that at  $45^{\circ}$  the more soluble hydrate is again the unstable one in contact with the solution.

*Prob. 40.* — By extending the appropriate curves on the diagram predict, *a*, at what temperature salt would begin to separate on cooling a 30%  $\text{Na}_2\text{HPO}_4$  solution in case the stable hydrate  $\text{AW}_{12}$  separates, and in case the solution remains supersaturated with respect to this hydrate; *b*, at what temperature the hydrate  $\text{AW}_{12}$  would melt if on heating its transition into  $\text{AW}_7$  and solution did not take place.

*Prob. 41.* — *Correlation of Vapor-Pressure-Temperature and Temperature-Composition Diagrams.* — With the aid of the diagram under consideration and that of Art. 120 determine and tabulate for the temperatures 20, 25, 30, 35.5 and 40° the vapor-pressures and percentage compositions of the saturated solutions and the nature of the solid phases with respect to which the solutions are saturated. (Note that the effect of pressure on the solubility is here neglected.)

Brief consideration may also be given to systems involving two liquid phases as well as solid phases. Such systems are occasionally met with among alloys, and frequently among non-metallic substances, such as bromine and water, or isoamyl alcohol and water, which are partially miscible with each other. Their relations are illustrated by the accompanying diagram for the two components lead and zinc. In this diagram the curves CD and DE represent the compositions, expressed in atomic percentages, of the two liquid phases in equilibrium with each other, and the curve BC represents the composition of solutions in equilibrium with zinc.



*Prob. 42. — Interpretation of Diagrams for Systems with Solid Phases and Two Liquid Phases.* — *a.* With the aid of the diagram state all that would happen on cooling from  $1000^{\circ}$  to  $300^{\circ}$  alloys containing 40 and 90 atomic percents of zinc. *b.* State all that would happen on gradually adding zinc to molten lead at  $350^{\circ}$ , at  $700^{\circ}$ , and at  $1000^{\circ}$ . *c.* Specify the phases in which the system exists when its composition and temperature are represented by any point within each of the fields, ABF, FB<sub>2</sub>H, CDE, BCEG, and BGKJ.

**122. Systems with Liquid and Gaseous Phases.** — Systems of two components having a gaseous phase and a liquid phase in which the components are miscible in all proportions have already been considered in Arts. 42 and 43. The boiling-point-composition diagrams of Art. 43, which are temperature-composition diagrams at one atmosphere, are further considered in Prob. 43 with reference to the significance of the fields.

The vapor-pressure relations of systems whose components have only limited miscibility in the liquid state were briefly considered in Art. 47.

*Prob. 43. — Temperature-Composition Diagrams.* — Reproduce in the form of separate sketches the three diagrams in the figure of Art. 43, and letter each of the fields so as to show the phases in which the system exists when its temperature and composition are represented by any point within the field.

**123. Systems Involving Solid Solutions.** — The components sometimes separate from a liquid solution in the form of solid solutions, instead of in the form of the pure solid substances or of solid compounds of them. By *solid solutions* are meant physically homogeneous solid mixtures of two or more substances, that is, solid mixtures which contain no larger aggregates than the molecules of the substances.

In their equilibrium relations solid solutions closely resemble liquid solutions; differing from them mainly in the respect that the equilibrium conditions are less readily established, owing to the restricted molecular motion characteristic of the solid state. It is often true in solid systems that equilibrium is not established and that the solid phases fail to attain the uniform composition corresponding to equilibrium, unless the systems are kept for a time at a high temperature or at a temperature not far below the melting-point, where the molecules still retain sufficient mobility. The purpose of the process of *tempering* or *annealing* solid substances is to allow time for the establishment of equilibrium at temperatures so high that it may be rapidly attained.

In solid solutions in which equilibrium is really attained, each

component lowers, as in liquid solutions, the vapor-pressure, solution-tendency, and mass-action or activity of the other component. As a result of these effects the freezing-point of a substance may be either raised or lowered by the addition of another substance, according as the solid solution which separates is more or less concentrated than the liquid solution, as is shown by the following problem.

*Prob. 44. — Raising of Freezing-Point by Solutes.* — The addition of benzene to thiophene raises the freezing-point of the thiophene, owing to the formation of solid solutions. *a.* Show how this can be accounted for by sketching a diagram, similar to that of Art. 48, representing the vapor-pressures of pure thiophene in the liquid and solid states and of a liquid solution of benzene in thiophene, and draw in on the sketch a line showing the vapor-pressure of thiophene at various temperatures in a solid solution of benzene and thiophene of the composition of that which separates from the liquid solution. *b.* Show that the mol-fraction of benzene must be greater in the solid solution than in the liquid solution in order that the freezing-point may be raised, provided Raoult's law holds for the solid solution as usually seems to be approximately true when the proportion of solute is small.

The two components are sometimes soluble in each other in the solid state in all proportions, forming a complete series of solid solutions. In most cases, however, each component has only a limited solubility in the other solid; so that two series of solid solutions result, each covering only a limited range of composition.

The temperature-composition diagrams representing the equilibrium conditions between solid solutions and liquid solutions correspond completely with those for liquid solutions and their vapors, since in both cases there are involved two phases of variable composition. Thus systems in which there are solid solutions containing the components in all proportions may have diagrams of any of the three types represented in the figure of Art. 43; two of which are illustrated by Probs. 45 and 46. Systems in which the components have only partial miscibility in the solid state are illustrated by Prob. 47, the diagram of which represents also certain other effects which have been already considered.

*Alloys with Complete Series of Solid Solutions. —*

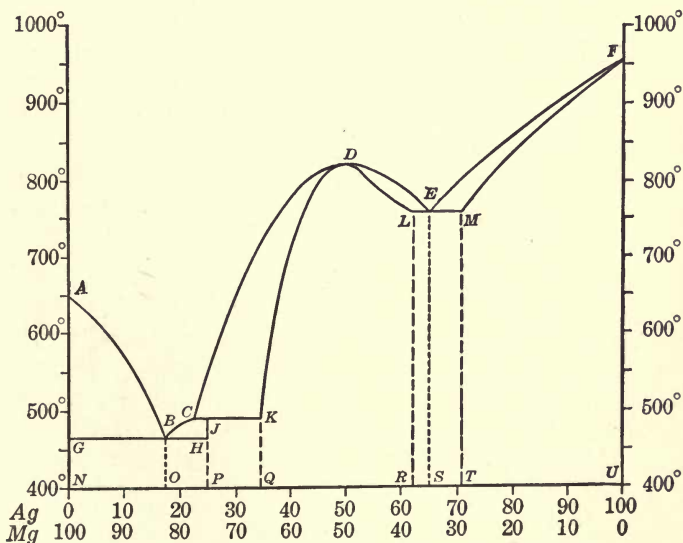
*Prob. 45.* — The cooling curves show that on cooling molten mixtures of nickel and copper solidification begins and becomes complete at the following temperatures, a solid solution separating in each case:

Percentage of nickel	0	10	40	70	100
Solidification begins	1083°	1140°	1270°	1375°	1452°
Solidification ends	1083°	1100°	1185°	1310°	1452°

*a.* Draw on a composition-temperature diagram two continuous curves corresponding to these data. Letter each field so as to show of what the system consists at any point. *b.* State what happens on slowly cooling a 50% mixture from  $1400^{\circ}$  to  $1200^{\circ}$ , giving the compositions of the liquid and solid solutions in equilibrium with each other at the temperatures at which solidification begins and ends, and at  $1275^{\circ}$ . (Note that the compositions of the liquid and solid solutions at any temperature are given by the points corresponding to that temperature on the upper and lower curves, since at any temperature the composition of the liquid phase is identical with that of a system from which at that temperature solid just begins to separate, and the composition of the solid phase is identical with that of a system which at that temperature just completely solidifies.)

*Prob. 46.* — Gold and copper form a complete series of solid solutions. The mixture containing 60 atomic percent gold has a constant melting-point of  $880^{\circ}$ . Gold melts at  $1063^{\circ}$ , and copper at  $1083^{\circ}$ . Sketch the temperature-composition diagram.

*Prob. 47.* — *Alloys Forming Compounds and Limited Series of Solid Solutions.* — In the figure, constituting the diagram for silver-magnesium alloys, in which the composition is expressed in atomic percentages,



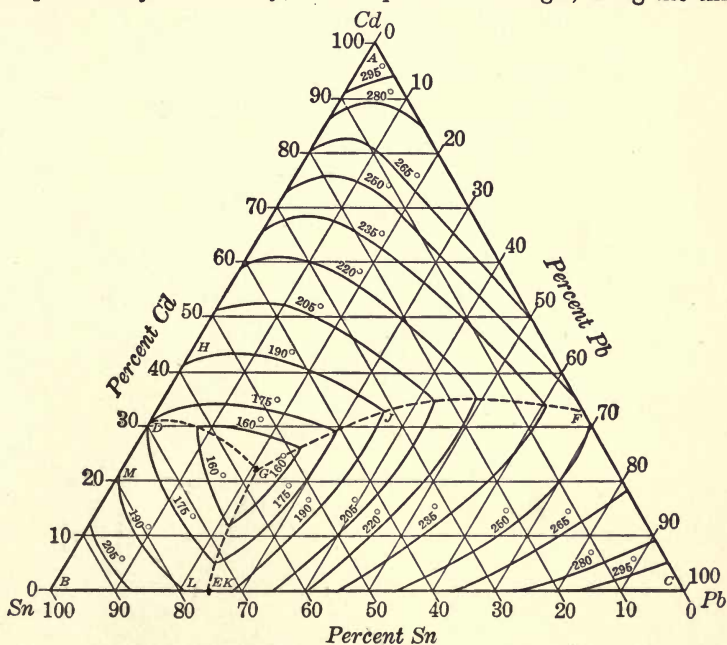
the curves KD, DL, and MF represent the composition of solid solutions in equilibrium with the liquid solutions whose composition is represented by the curves CD, DE, and EF, respectively. *a.* State what equilibria are represented by the curves AB and BC. *b.* State what compounds are indicated by the diagram. *c-h.* State what

happens on cooling slowly till complete solidification results a liquid mixture containing the following atomic percentages of silver: *c*, 90; *d*, 70; *e*, 55; *f*, 50; *g*, 25; *h*, 20. *i*. Specify the phases in which the system exists when its composition and temperature are represented by any point in each of the fields CKD, DLE, EMF, QKDLR, RLMT, and BCJH.



## V. THREE-COMPONENT SYSTEMS

**124. Systems with Liquid and Solid Phases. Temperature-Composition Diagrams.** — In systems of three components existing in one solid phase and one liquid phase the composition is not determined by specification of the pressure and temperature, but becomes definite when the percentage or mol-fraction of one of the components is also specified. With such systems there must therefore be employed diagrams which show how the percentages or mol-fractions of the three components are related to one another. The most common form of diagram, one which has the advantage of treating the three components symmetrically, is an equilateral triangle, along the three



sides of which are plotted the atomic percentages or mol-fractions of the three components, as in the above figure. In such a diagram the vertices then represent the pure components, points on the sides represent mixtures of each pair of components, and points within the triangle represent mixtures of all three components. Thus the upper vertex would represent pure cadmium; the point H, a mixture consisting of 42% of Cd and 58% of Sn; and the point G, a mixture consisting of 22% of Cd, 57% of Sn, and 21% of Pb.

At any one temperature the various compositions of the liquid phase with which any definite solid phase is in equilibrium are represented on such a diagram by a line. Thus the lines HJ, JK, and LM represent at  $190^{\circ}$  the compositions of the liquid with which solid cadmium, solid lead and solid tin, respectively, are in equilibrium. The point J then evidently represents the composition of the liquid with which the two solid phases Cd and Pb are in equilibrium at  $190^{\circ}$ . Similar lines can be drawn corresponding to various other temperatures, thus giving a series of isotherms representing the effect of temperature on the equilibrium of the phases. The dotted line FG evidently shows the variation with the temperature of the composition of the liquid phase in equilibrium with the two solid phases Cd and Pb; the line DG shows the same thing for the two solid phases Cd and Sn; and the line EG for the two solid phases Sn and Pb. And the point G shows the only temperature and liquid composition at which the three solid phases Cd, Pb, and Sn coexist in equilibrium with the liquid phase. The mixture of three solid phases separating at this point is called the *ternary eutectic*, and the point itself the *ternary eutectic point*.

A more complete representation of the effect of temperature is secured by plotting temperatures along an axis perpendicular to the plane of the composition triangle. A model in the form of a triangular prism thus results, whose horizontal sections are the isotherms represented in a plane triangular diagram, like that in the figure.

*Prob. 48. — Behavior of a Liquid Ternary Alloy on Cooling Predicted from its Temperature-Composition Diagram.* — A completely liquid mixture of 50 Cd, 30 Sn, and 20 Pb is cooled till it wholly solidifies. *a.* State the temperature at which solidification begins and the nature of the solid phase which then separates. *b.* State the direction on the diagram which on further cooling the changing composition of the liquid phase follows. (Note that the separation of the solid phase does not change the ratio of the atomic quantities of the other two components in the liquid phase.) *c.* State the temperature at which a second solid phase begins to separate, the composition of the liquid phase, and the nature of the solid phase. *d.* Describe what happens on further cooling. *e.* Describe the texture of the solid alloy.

**125. Systems with Gaseous, Liquid, and Solid Phases in Relation to the Phase Rule and Mass-Action Law.** — Three-component systems existing in gaseous, liquid, and solid phases will be here considered only with reference to the phase rule, and incidentally to the mass-action law in order to show the relations between these two principles.

*Applications of the Phase Rule and Mass-Action Law. —*

*Prob. 49. — a.* Show by the equilibrium laws applicable to dilute solutions how the solubility of  $\text{CaCO}_3$  in water saturated with  $\text{CO}_2$  gas at a given temperature is quantitatively related to the pressure of the  $\text{CO}_2$  gas, considering that the salt in the solution is substantially all  $\text{Ca}^{++}(\text{HCO}_3^-)_2$ . *b.* Show that the phase rule requires that the solubility of  $\text{CaCO}_3$  in water saturated with  $\text{CO}_2$  gas is definitely determined when the pressure and temperature are specified.

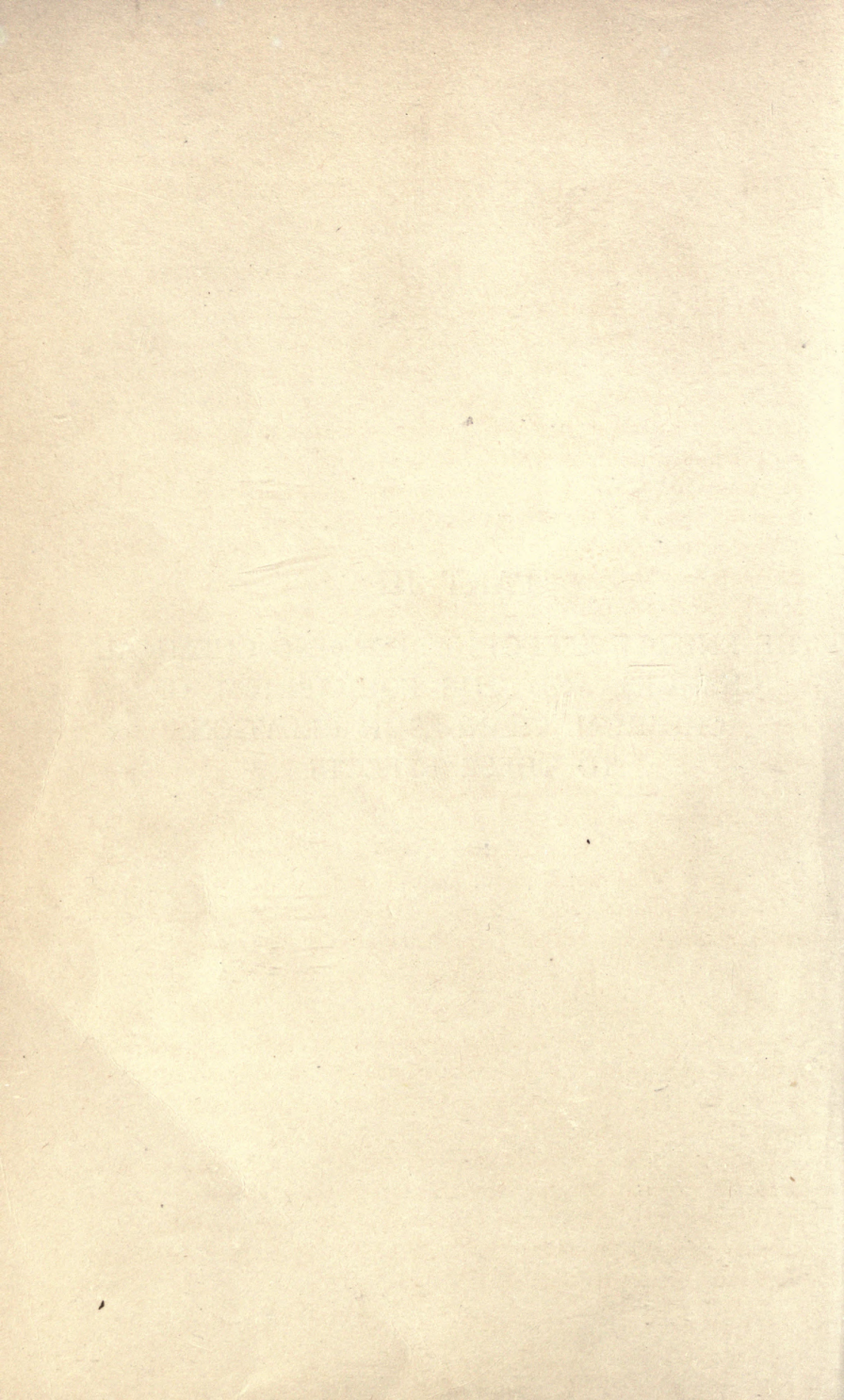
*Prob. 50. —* Silver chloride forms with ammonia two solid compounds  $\text{AgCl} \cdot \frac{1}{2}\text{NH}_3$  and  $\text{AgCl} \cdot 3\text{NH}_3$ , which exist in contact with aqueous solutions. Determine by the phase rule the variance of systems in which the following phases are present, and illustrate what this variance signifies by specifying in each case factors that would determine the state of the system: *a.* solid  $\text{AgCl}$ , aqueous  $\text{NH}_3$  solution, vapor; *b.* solid  $\text{AgCl}$ , solid  $\text{AgCl} \cdot \frac{1}{2}\text{NH}_3$ , solution, vapor; *c.* solid  $\text{AgCl}$ , solid  $\text{AgCl} \cdot \frac{1}{2}\text{NH}_3$ , solid  $\text{AgCl} \cdot 3\text{NH}_3$ , solution, vapor. *d.* At  $25^\circ$  ammonia vapor is in equilibrium with the solids  $\text{AgCl}$  and  $\text{AgCl} \cdot \frac{1}{2}\text{NH}_3$  at 10 mm. and with the solids  $\text{AgCl} \cdot \frac{1}{2}\text{NH}_3$  and  $\text{AgCl} \cdot 3\text{NH}_3$  at 105 mm. State under what conditions each of these two pairs of solid phases would exist in equilibrium with an aqueous solution. *e.* With the aid of the data of Prob. 23, Art. 39, determine the concentration of free  $\text{NH}_3$  in the aqueous solution at which  $\text{AgCl}$  is converted into  $\text{AgCl} \cdot \frac{1}{2}\text{NH}_3$  at  $25^\circ$ . *f.* Assuming that the  $\text{AgCl}$  in the solution is substantially all in the form of completely ionized  $\text{Ag}(\text{NH}_3)_2^+ \text{Cl}^-$ , derive from the equilibrium laws of dilute solutions a relation between the solubility  $s$  of  $\text{AgCl}$  and the partial pressure  $p$  of  $\text{NH}_3$  in the vapor, first, when the solid phase is  $\text{AgCl}$ , and secondly, when it is  $\text{AgCl} \cdot \frac{1}{2}\text{NH}_3$ .

The preceding problems illustrate the characteristic differences between the conclusions to be drawn from the phase rule and from the mass-action law. The phase rule is qualitative, its application presupposes no special knowledge beyond that of the number of components and phases, and it is applicable without any limitation of concentration. The mass-action law is quantitative, its application presupposes knowledge of the molecular species present, and, if numerical values are to be computed, also of their dissociation-constants; and it is applicable in exact form only to solutions or gases at small concentrations.



PART III

THE ENERGY EFFECTS ATTENDING CHEMICAL  
CHANGES, AND THE EQUILIBRIUM OF  
CHEMICAL CHANGES IN RELATION  
TO THESE EFFECTS



## CHAPTER IX

### THE PRODUCTION OF HEAT BY CHEMICAL CHANGES

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#### I. THE FUNDAMENTAL PRINCIPLES OF THERMOCHEMISTRY

**126. The First Law of Thermodynamics.** — The branch of chemistry dealing with the heat-effects and changes in energy-content attending chemical changes is called *thermochemistry*. The first section of this chapter is devoted to a consideration of the fundamental principles underlying the subject and of the methods of determining and expressing thermochemical quantities. In the second section of the chapter are presented some of the more important generalizations derived from the results of thermochemical measurements.

The general principles relating to energy which form the basis of thermochemistry have already been considered in Arts. 23 to 25. It will suffice to recall here the following fundamental laws derived from the law of the conservation of energy:

(1) The energy-content  $U$  of a system is fully determined by the state of the system; and correspondingly, the change in the energy-content of a system attending any change in its state is determined solely by the initial and final states of the system irrespective of the process by which the change in state takes place.

(2) The decrease  $U_1 - U_2$  in the energy-content of a system attending any change in its state is equal to the sum of the quantities of heat  $Q$  and work  $W$  produced in the surroundings.

These principles constitute the *first law of thermodynamics*. They are expressed by the following equation known as the *first-law equation*:

$$U_1 - U_2 = Q + W.$$

It will be noted that, though the change in energy-content is definite for a specified change in state, the relative quantities of heat and work produced may vary with the process by which the change in state is brought about. The change in energy-content is therefore the more fundamental quantity.

The law of initial and final states is constantly employed in thermochemistry to calculate the heat-effects attending chemical changes that do not take place under conditions which make possible exact calorimetric measurements. This is illustrated by Prob. 1 below and more fully by the problems of Art. 130.

*Prob. 1. — Calculation of Heat of Reactions with Aid of the Law of Initial and Final States.* — When at  $20^{\circ}$  12 g. of graphite are burned with oxygen to form  $\text{CO}_2$  at  $20^{\circ}$  within a closed vessel so that no work is produced, 94,200 cal. are evolved; and when 28 g. of CO are so burned with oxygen, 68,000 cal. are evolved. Show by the law of initial and final states how the heat evolved by the burning of 12 g. of graphite to CO at  $20^{\circ}$  within a closed vessel can be calculated.

The relations between energy-content, heat, and work were illustrated in Prob. 38, Art. 23, by applying them to the phenomenon of vaporization. They are applied to a chemical change in Prob. 5, Art. 128.

**127. Heat-Effects Attending Isothermal Changes in State.** — The heat-effect attending a change in the state of a system at a constant temperature is ordinarily experimentally determined by a combination of the following processes. The change in state is first caused to take place within a calorimeter (as nearly as possible) adiabatically; and the change in temperature of the calorimeter is exactly measured. The quantity of heat which must be imparted to or withdrawn from the calorimeter and its contents to restore them to the initial temperature is then accurately determined, either by direct measurement or by calculation from the known heat-capacities of the substances present. This quantity of heat is evidently equal to the heat-effect that would attend the change in state if it took place isothermally at the initial temperature. This method is illustrated in principle by the following problem.

*Prob. 2. — Experimental Determination of the Heat-Effects Attending Isothermal Changes in State.* — Into a calorimeter containing  $50\text{H}_2\text{O}$  at  $20.00^{\circ}$  1KCl at  $20.00^{\circ}$  is introduced, and the temperature falls to  $15.11^{\circ}$ . *a.* What change in state takes place in this process, considering the calorimeter to be a part of the system; and what is the heat-effect, assuming that any loss of heat by radiation has been corrected for? *b.* What change in state takes place when 1KCl is dissolved in  $50\text{H}_2\text{O}$  at  $20^{\circ}$  and the resulting solution is brought to  $20^{\circ}$ ? *c.* In order to calculate the heat-effect attending this change in state, what other change in state must be combined with that occurring in the calorimeter? *d.* Calculate the value of this heat-effect with the aid of such of the following data as may be needed: the heat-capacity of the calorimeter is 19 cal. per degree; the specific heat-capacity of solid potassium chloride is 0.166, of water is 1.00, and that of the solution of 1KCl in  $50\text{H}_2\text{O}$  is 0.904 cal. per degree.

Changes in state at constant temperature may take place without change of volume or without change of pressure. The different heat-

effects attending these two different changes in state are known as the *heat-effect at constant volume*  $Q_v$  and the *heat-effect at constant pressure*  $Q_p$ .

The heat-effect at constant pressure is the one which is usually called the *heat of reaction*, and the one which is commonly recorded in tables of constants. There is difference of usage regarding the algebraic sign of the heat of reaction: when heat is actually evolved by the reaction, the heat of reaction is usually taken positive in thermochemical considerations, but negative in thermodynamic considerations. In this book a uniform convention, corresponding to the thermochemical one, is employed throughout; heat-effects being always considered positive when heat is evolved, as in the combustion of hydrogen and oxygen, and negative when it is absorbed from the surroundings, as in the vaporization of water.

The law that the energy-content of a perfect gas at a definite temperature is independent of its pressure (Art. 26) leads to the conclusion that in the case of reactions involving perfect gases the heat-effect  $Q_v$  at constant volume is greater than the heat-effect  $Q_p$  at constant pressure by an amount equal to the work produced when the reaction takes place at constant pressure. This work can readily be shown to be equal to  $(N_2 - N_1)RT$ , where  $N_2$  denotes the number of mols of gaseous substances present in the final state, and  $N_1$  the number in the initial state. That is,  $Q_v = Q_p + (N_2 - N_1)RT$ . The derivation and application of this principle are illustrated by the following problems.

*Prob. 3. — Relation between the Heats of Reaction of Gaseous Substances at Constant Pressure and Constant Volume.* — Show that  $RT$  is the difference between the quantities of heat evolved when at  $T$  two mols of CO and one mol of  $O_2$  at 1 atm. unite to form  $CO_2$  in one case at constant pressure (for example, in an open calorimeter); and in another case at constant volume (for example, in a bomb calorimeter). Note that the change of state which results when the reaction takes place at a constant pressure of 1 atm. could also be brought about by a process consisting of two steps, namely, by causing the mixture of CO and  $O_2$  at 1 atm. to change at constant volume to  $CO_2$  (whereby the pressure would become  $\frac{2}{3}$  atm.), and then compressing it till its pressure becomes 1 atm.

*Prob. 4. — Heats of Combustion at Constant Pressure and Constant Volume.* — When 1 formula-weight of solid naphthalene ( $C_{10}H_8$ ) is burnt with oxygen at  $20^\circ$  in a bomb calorimeter 123,460 cal. are evolved. Calculate its heat of combustion at constant pressure.

**128. Change in Energy-Content and in Heat-Content.** — The decrease in the energy-content attending any change in the state of a system is found simply by adding together the heat evolved and the

work produced in any process by which that change is brought about.

When the change in state takes place at constant volume, no work is involved, and therefore the heat  $Q_v$  imparted to the surroundings is equal to the decrease  $U_1 - U_2$  in the energy-content of the system. When, on the other hand, the change takes place at constant pressure, there is not only a quantity of heat  $Q_p$  imparted to the surroundings, but also a quantity of work produced in them equal to  $p(v_2 - v_1)$ , as shown in Art. 24. The decrease  $U_1 - U_2$  in the energy-content of the system is then equal to  $Q_p + p(v_2 - v_1)$ .

Instead of determining and recording the values of  $U_1 - U_2$  for various changes of state, it is generally more convenient to employ the values of the quantity  $(U_1 + p_1 v_1) - (U_2 + p_2 v_2)$ . The quantity  $U + p v$ , like the quantity  $U$ , is a property of the system which always has a definite value when the system is in a definite state, and which always changes in value by a definite amount when the system changes from one state to another, whatever be the process by which the change in state is brought about; for it is evident that the pressure  $p$  and the volume  $v$ , as well as the energy-content  $U$ , have values which are determined by the state of the system. In other words, a law of initial and final states applies to the change in the quantity  $U + p v$ , just as it does to the change in the quantity  $U$ . For brevity, this quantity  $U + p v$  will be represented by a single letter  $H$ , and will be called the *heat-content* of the system; it being understood that this term is a purely conventional one which does not imply that the energy quantity denoted by it is a heat quantity, any more than the term energy-content implies it.

The relation between the decrease in heat-content and the decrease in energy-content attending any change in state is evidently expressed by the equation:

$$H_1 - H_2 = U_1 - U_2 + p_1 v_1 - p_2 v_2.$$

Or writing, as will be done throughout the remainder of this book,  $-\Delta H$ ,  $-\Delta U$ ,  $-\Delta(pv)$ ,  $-\Delta N$ , etc., for the decrease in the value of any quantity attending any change in state, that is, for the difference between its value in the initial state (denoted by subscript 1) and its value in the final state (denoted by subscript 2), this equation may be written in the form

$$-\Delta H = -\Delta U - \Delta(pv).$$

Substituting for  $-\Delta U$  the expression for it given by the first-law equation, there results

$$-\Delta H = Q + W - \Delta(pv).$$

For a change in state for which the initial pressure  $p_1$  and the final pressure  $p_2$  have the same value  $p$  the decrease in heat-content is equal to the heat evolved when the change takes place at the constant pressure  $p$ ; for the work  $W$  produced in this process is  $p(v_2 - v_1)$  and hence equal to  $\Delta(pv)$ . That is,  $-\Delta H = Q_p$ , where  $Q_p$  is the heat of reaction at constant pressure.

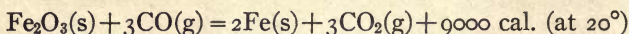
The fact that the decrease of heat-content is equal to the commonly considered heat of reaction at constant pressure is one of the important reasons for employing the heat-content, instead of the energy-content, in thermochemical and thermodynamic considerations. Another advantage in using heat-content is that it makes it unnecessary to evaluate the change in volume attending the change in state. The employment of heat-content is preferable also because it is related more closely than the energy-content to the concept of free energy considered in the next chapter, and because many of the thermodynamic relations assume a simpler form when heat-content and free energy are employed.

The relations between energy-content or heat-content and the quantities of heat and work produced are illustrated by the following problem.

*Prob. 5. — Calculation of Changes in Heat-Content and Energy-Content from the Heat and Work Produced. — a.* When the reaction  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$  takes place without change of temperature or pressure in a system consisting of 2 mols of CO and 1 mol of  $\text{O}_2$  at  $20^\circ$  and 1 atm., 136,000 cal. are evolved. What is the decrease in the heat-content, and what is the decrease in the energy-content, of the system? *b.* When the reaction takes place in the same mixture without change of temperature or volume 135,420 cal. are evolved. What is the decrease in the heat-content, and what is the decrease in the energy-content in this case? *c.* In what respect does the final state of the system in *a* differ from that in *b*, and what principle previously considered accounts for the fact that the changes in energy-content or in heat-content are equal in the two cases.

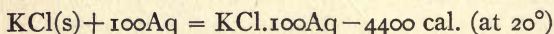
**129. Expression of Changes in Heat-Content by Thermochemical Equations.** — In order to express the changes in heat-content that attend changes in state, especially those involving chemical reactions, at any constant temperature and pressure, equations are conveniently

employed in which the heat-contents of the various substances involved are represented by their chemical formulas, and in which the change in heat-content is shown by placing a numerical term on the right-hand side of the equation. For example, the expression



signifies that at  $20^\circ$  and 1 atm. (this pressure being understood unless some other pressure is stated) the heat-content of one formula-weight of solid ferric oxide plus that of three formula-weights of gaseous carbon monoxide is equal to the heat-content of two formula-weights of solid iron plus that of three formula-weights of gaseous carbon dioxide plus 9000 cal.; 9000 cal. being the decrease ( $-\Delta H$ ) in the heat-content of the system, which is equal to the heat evolved by the system when the reaction takes place at a constant temperature and pressure. Such expressions are called *thermochemical equations*, or specifically, *heat-content equations*.

As indicated in the preceding equation, the states of aggregation of substances are shown by affixing to the formulas letters within parentheses, as stated in Art. 109. The fact that a substance is dissolved in  $x$  formula-weights of water is shown by attaching the symbol  $x\text{Aq}$  to the formula of the substance. Thus the equation



signifies that when at  $20^\circ$  one formula-weight of solid potassium chloride is dissolved in 100 formula-weights of water there is an increase of 4400 cal. in the heat-content of the system, corresponding to an absorption of 4400 cal. from the surroundings. When the substance is dissolved in so large a quantity of water that the addition of more water produces no appreciable heat-effect, the symbol  $\infty\text{Aq}$  may be attached to the formula of the substance.

These thermochemical equations can be treated strictly as algebraic equations, and can be combined with one another by addition or subtraction; for every quantity in them has a definite value (namely, that of the heat-content of the substance represented by the formula), irrespective of the other quantities that occur with it in the equations.

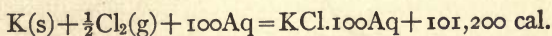
*Expression of Heat Data and Calculation of Heats of Reactions by Thermochemical Equations. —*

✓ *Prob. 6.* — The union at  $20^\circ$  and 1 atm. of 1 g. of aluminum with oxygen is attended by a heat-evolution of 7010 cal.; and the union of 1 g. of graphite with oxygen to form carbon monoxide is attended by a heat-evolution of 2160 cal. Express these data in the form of thermo-

chemical equations; and calculate from them the heat of the reaction  $\text{Al}_2\text{O}_3(\text{s}) + 3\text{C}(\text{s}) = 2\text{Al}(\text{s}) + 3\text{CO}(\text{g})$  at  $20^\circ$ .

*Prob. 7. — a.* Express the following data in the form of thermochemical equations, employing the conventions described in the preceding text. The heat of formation of 1 mol of gaseous HCl from the elementary substances is 22,000 cal. Its heat of solution in 100 formula-weights of water is 17,200 cal. The heat of the reaction between 1 mol of gaseous chlorine and a solution of 2 formula-weights of HI in 200 formula-weights of water, forming solid iodine and a dilute HCl solution is 52,400 cal. The heat of solution of 1 mol of gaseous HI in 100 formula-weights of water is 19,200 cal. *b.* By combining these equations calculate the heat of formation of 1 mol of gaseous HI from gaseous hydrogen and solid iodine.

Although it is true that only *changes* in heat-content can be determined, yet it is convenient to employ an arbitrary scale of heat-content which has as its zero-points the heat-contents of the various elementary substances at the temperature under consideration, at a pressure of one atmosphere, and in the form which is most stable at this temperature and pressure. Under this convention the heat-content ( $H$ ) of any compound substance is evidently equal to the increase in heat-content ( $\Delta H$ ) which attends its formation out of the elementary substances; and in any thermochemical equation the formula of a substance may evidently be replaced by the numerical value of its heat of formation with opposite sign. For example, the heat-content at  $20^\circ$  of one formula-weight of gaseous hydrogen bromide, or the numerical value of the formula  $\text{HBr}(\text{g})$  is  $-8500$  cal.; for 8500 cal. is the heat evolved when it is formed out of gaseous hydrogen and liquid bromine at  $20^\circ$  and 1 atmosphere. Similarly the heat-content of a potassium chloride solution represented by the formula  $\text{KCl.100Aq}$  is  $-101,200$  cal.; for 101,200 cal. is the sum of the heat (105,600 cal.) evolved when one formula-weight of solid KCl is formed out of solid potassium and gaseous chlorine at  $20^\circ$  and of the heat ( $-4400$  cal.) evolved when it is dissolved in 100 formula-weights of water at  $20^\circ$ . The heat of formation of this solution is expressed by the equation



This example shows that in thermochemical equations the symbol  $x\text{Aq}$  (not attached to another formula) has, like the formulas of elementary substances, the value zero; for the water represented by it has not been formed out of its elements. Water which has been so formed is represented by the formula  $x\text{H}_2\text{O}$ .

It is evident that the employment of heats of formation greatly simplifies the task of determining and systematizing thermochemical data; for, instead of measuring and recording the change in heat-content attending every chemical reaction, it suffices to do this for the formation of every compound out of the corresponding elementary substances. The numerical values of the heats of formation so determined, which will be found recorded in tables of physical and chemical constants, like those of Landolt-Börnstein, may then be substituted in any thermochemical equation, and the change in heat-content attending the corresponding reaction may thus be calculated.

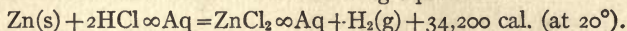
*Prob. 8. — Calculation of Heat of Reaction from Heats of Formation. —* Calculate the heat-effect that attends at  $20^{\circ}$  the chemical reaction  $\text{PbS(s)} + 2\text{PbO(s)} = 3\text{Pb(s)} + \text{SO}_2\text{(g)}$  from the following heats of formation at  $20^{\circ}$ :  $\text{PbO(s)}$ , 50,300 cal.;  $\text{PbS(s)}$ , 19,300 cal.;  $\text{SO}_2\text{(g)}$ , 70,200 cal.

**130. Indirect Determination of the Heat-Effects of Chemical Changes.** — On account of radiation errors the heat-effect can be directly determined by calorimetric measurements only for those chemical changes which take place completely within a few minutes, and for such changes only when the temperature is not greatly different from the room temperature. It is, however, possible to calculate the heat-effects of many other changes at or near the room temperature from those which have been directly measured, by applying the law of initial and final states. This has already been exemplified in the preceding articles, and it is more fully illustrated by the following problems. The indirect method commonly employed for determining heat-effects at temperatures much higher or lower than the room temperature is described in the next article.

*Derivation of Heats of Formation. —*

*Prob. 9. —* At  $20^{\circ}$  the heat of combustion of one mol of acetylene ( $\text{C}_2\text{H}_2$ ) is 313,000 cal. Calculate its heat of formation. The heat of formation of  $1\text{H}_2\text{O(l)}$  is 68,400 cal., and that of  $1\text{CO}_2\text{(g)}$  from graphite and oxygen is 94,200 cal.

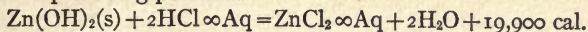
*Prob. 10. — a.* State just what heats of formation are denoted by the second and third terms in the following equation:



*b.* Write the complete thermochemical equations which express these heats of formation, taking into account the facts that the heat of formation of 1 mol of gaseous HCl is 22,000 cal. and that its heat of solution in a large quantity of water is 17,300 cal.

*Prob. 11. —* Calculate the heat of formation of  $1\text{Zn(OH)}_2\text{(s)}$  from the

following equation and from the other necessary data, which have been given in preceding problems:



*Prob. 12.* — Calculate the heat of formation at  $20^\circ$  of  $\text{H}_2\text{SO}_4(\text{l})$  from the following data at  $20^\circ$  and those given in preceding problems. The heat of solution in a large quantity of water of  $\text{SO}_2(\text{g})$  is 8000 cal., and that of  $\text{H}_2\text{SO}_4$  is 18,000 cal. One mol of gaseous  $\text{Cl}_2$  acting on a dilute solution of 1 mol of  $\text{SO}_2$  with formation of a dilute solution of  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  produces a heat-evolution of 73,900 cal. (Note that when  $x$  formula-weights of  $\text{H}_2\text{O}$  are involved in the chemical reaction the symbol  $x\text{H}_2\text{O}$  must appear in the thermochemical equation, even though  $\infty \text{Aq}$  may also occur in it.) *Ans.* 192,300 cal.

*Indirect Determination of Heats of Reaction.* —

*Prob. 13.* — A direct determination of the heat-effect of the reaction  $\text{CH}_3\text{CH}_2\text{OH} \infty \text{Aq} + \text{O}_2(\text{g}) = \text{CH}_3\text{CO}_2\text{H} \infty \text{Aq} + \text{H}_2\text{O}$  is not practicable. State what measurements could be made which would enable this heat-effect to be calculated; and show how it would be calculated from the results of such measurements.

*Prob. 14.* — Suggest a series of chemical reactions from whose heat-effects, which must be readily determinable in a calorimeter, the heat of formation of  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(\text{s})$  at  $20^\circ$  could be calculated. Write the thermochemical equations, and indicate how they would be combined to yield the desired result.

**131. Influence of Temperature on the Heat-Effects Attending Chemical Changes.** — The heat-effect at constant pressure of a chemical change taking place at any temperature can be derived from the heat-effect at constant pressure at any other temperature by the following consideration of two different processes resulting in the same change in state. In one process cause the chemical change (for example, the union of 1 mol of  $\text{CO}$  with  $\frac{1}{2}$  mol of  $\text{O}_2$ ) to take place at pressure  $p$  and temperature  $T_1$ , and heat the products (the carbon dioxide) under the pressure  $p$  to the other temperature  $T_2$ ; and, in the second process, heat the reacting substances (the carbon monoxide and oxygen) under the pressure  $p$  from  $T_1$  to  $T_2$ , and cause them to combine (forming carbon dioxide) at the pressure  $p$  and the temperature  $T_2$ . Since in each of these processes the system changes from the same initial state (1 mol of  $\text{CO}$  and  $\frac{1}{2}$  mol of  $\text{O}_2$  at  $p$  and  $T_1$ ) to the same final state (1 mol of  $\text{CO}_2$  at  $p$  and  $T_2$ ), the total change in heat-content must be the same in the two processes; and therefore the heat evolved at the temperature  $T_2$  must differ from the heat evolved at the temperature  $T_1$  by the same amount as the heat absorbed in heating the reacting substances differs from that absorbed in heating the reaction-products from  $T_1$  to  $T_2$  at the constant pressure  $p$ .

*Effect of Temperature on Heat of Reaction. —*

*Prob. 15. — a.* Represent on a diagram, in which the ordinates denote the temperature, and the abscissas the heat-content of the system, how the heat-content changes during each step of the two processes described in the text for bringing about the change in state,  $1\text{CO} + \frac{1}{2}\text{O}_2$  at  $T_1$  and  $p$  to  $1\text{CO}_2$  at  $T_2$  and  $p$ . Make the arbitrary assumption that the heat-content of the system in the initial state is zero. *b.* With the aid of the diagram formulate an algebraic relation between the heats of reaction  $Q_{T_2}$  and  $Q_{T_1}$  at the two temperatures  $T_2$  and  $T_1$  and the heat-capacities  $C_1$  and  $C_2$  of the system in its initial and final states respectively. *b.* Noting that this relation is exact only when the heat-capacities do not vary with the temperature, formulate an exact differential expression, and also an integral which is a general expression for the difference in the heats of reaction at two temperatures, when no change takes place in the state of aggregation between those temperatures.

*Prob. 16. —* Calculate the heat of formation of  $1\text{PbO(s)}$  at  $200^\circ$  from its heat of formation ( $50,300$  cal.) at  $20^\circ$  and from the specific heat-capacities at constant pressure of lead ( $0.032$ ), of oxygen ( $0.212$ ), and of lead oxide ( $0.052$ ). *Ans.*  $50,000$  cal.

*Prob. 17. —* Calculate the heat of formation of  $1\text{H}_2\text{O(g)}$  at  $1000^\circ$  from the following data. The heat of formation of  $1\text{H}_2\text{O(l)}$  at  $20^\circ$  is  $68,400$  cal. Its heat of vaporization at  $100^\circ$  is  $-9,670$  cal. The molal heat-capacity at constant pressure at  $T$  is  $6.69 + 0.0007T$  for oxygen,  $6.54 + 0.0007T$  for hydrogen, and  $8.81 - 0.0019T + 0.000,002,22T^2$  for water-vapor. *Ans.*  $59,800$  cal.

## II. GENERAL RESULTS OF THERMOCHEMICAL INVESTIGATIONS

**132. Heat-Effects Attending Changes in the State of Aggregation of Substances.** — The *heat of vaporization* of liquid substances, the *heat of fusion* of solid substances, and the *heat of transition* of one solid substance into another (as of rhombic into monoclinic sulfur) are quantities which are important in themselves and which are frequently involved in calculations of the heat of chemical reactions. The general statement can be made in regard to them that the conversion of the form that is stable at lower temperatures into that stable at higher temperatures (for example, of ice into water, or of rhombic into monoclinic sulfur) is always attended by an absorption of heat.

The following simple principle, known as *Trouton's rule*, has been discovered in regard to the values of the heat of vaporization. The ratio of the molal heat of vaporization of a liquid at its boiling-point to its boiling-point on the absolute scale has approximately the same value (namely, about  $-20.5$ ) for all liquids, except those whose molecules are associated; that is,  $\Delta\tilde{H}/T = \text{approx. } 20.5$ . The actual values of these quantities in the case of five very different liquids are shown in the following table.

HEATS OF VAPORIZATION AND TROUTON'S RULE

Substance	$\Delta\tilde{H}$	$T$	$\Delta\tilde{H}/T$
Bromine	6760	332	20.4
Benzene	7350	353	20.8
Carbon bisulfide	6380	319	20.0
Ethyl ether	6260	308	20.3
Ethyl formate	7180	327	22.0

Substances containing the hydroxyl group, such as water, alcohols, and acids, whose molecules in the liquid state are for other reasons believed to be associated (see Art. 38), form marked exceptions to Trouton's rule. Thus the value of  $\Delta\tilde{H}/T$  is 25.9 for water, 27.0 for ethyl alcohol, and 14.9 for acetic acid.

The molal heat of vaporization of a liquid or solid substance can be accurately calculated by the Clapeyron equation (Art. 33) from the change of its vapor-pressure with the temperature.

The *heat of solution* of substances is another important quantity. In determining and expressing it the quantity of solvent in which a definite weight of the substance is dissolved must be taken into consideration. The two limiting cases are the heats of solution in a very large quantity of solvent and in that quantity of solvent which forms

with the substance a saturated solution. These two heat-effects sometimes have different signs. They evidently differ by the heat of dilution of the saturated solution with a large quantity of water.

The dissolving of gaseous substances in solvents is always attended by an evolution of heat; and the dissolving of solid substances in solvents is usually attended by an absorption of heat. The mixing of liquids may be attended either by evolution or absorption of heat, as explained in Art. 42.

The *heat of dilution* of substances in solution is also important; for it enables the heat of formation of a solution of one concentration to be calculated from that of a solution of another concentration, and thus enables heats of reaction to be calculated at different concentrations. The heat-effect attending the addition of an equal volume of water to a concentrated aqueous solution is often large; but it becomes less as the concentration diminishes; and, after a moderately small concentration (such as 0.2 normal) has been attained, there is usually only a very small heat-effect on adding even a very large quantity of water. For example, on adding at 18° to 1 formula-weight of gaseous HCl or of solid ZnCl<sub>2</sub> successively  $\Delta N$  formula-weights of water, there are evolved the following quantities of heat ( $Q$ ) in calories:

$\Delta N$ . . . . .	5	5	10	30	50	100	200
$Q$ for HCl . . . .	14960	1200	600	360	120	50	..
$Q$ for ZnCl <sub>2</sub> . . .	7740	1850	1300	2170	1490	820	390

*Prob. 18. — Heat of Transition Derived from Heats of Solution.* — The heat of solution at 20° in a large quantity of chloroform of 1 at. wt. of rhombic sulfur is -640 cal. and of 1 at. wt. of monoclinic sulfur is -560 cal. Show, by applying the law of initial and final states, what other heat-effect can be derived from these data, and what its value is.

*Prob. 19. — Change of Heat of Reaction with the Concentration.* — The heat of solution at 18° of 1Zn(s) in HCl.200Aq is 34,200 cal. Find its heat of solution in HCl.5Aq,  $a$ , by applying the law of initial and final states, and  $b$ , by formulating the thermochemical equations involved.

**133. Heats of Reaction in Aqueous Solution.** — The investigations made of the heat-effects attending chemical reactions in aqueous solution between substances present at fairly small concentrations (0.1-0.3 normal) have established the following principles:

(1) On mixing solutions of two neutral salts which do not form a precipitate by metathesis (for example, solutions of potassium chloride and sodium sulfate) there is scarcely any heat-effect. Exceptions to

this principle are met with in the few cases in which a unionized salt is produced by the metathesis. Thus the metathetical reaction  $2\text{K}^+\text{Cl}^- + \text{Hg}^{++}(\text{NO}_3^-)_2 = 2\text{K}^+\text{NO}_3^- + \text{HgCl}_2$  is attended by a heat-evolution of 12,400 cal.

(2) The heat of neutralization of a solution of any largely ionized monobasic acid with a solution of any largely ionized monacidic base (for example, of hydrochloric acid, nitric acid, etc., with sodium hydroxide, potassium hydroxide, etc.) has approximately the same value, whatever be the acid or base. At 18° this nearly constant value averages 13,800 cal. per equivalent when the acid and base solutions are 0.12 to 0.25 normal.

(3) When the base or acid is only partly ionized (as in the case of ammonium hydroxide or hydrofluoric acid), the heat-effect attending its neutralization with a largely ionized acid or base is often much larger or smaller than that observed when both acid and base are largely ionized; thus the heat of neutralization of one equivalent of ammonium hydroxide with one of hydrochloric acid is 12,300 cal., and that of one equivalent of hydrofluoric acid with one of sodium hydroxide is 16,300 cal.

(4) When one formula-weight of a dibasic acid is neutralized in steps by adding first one equivalent of a largely ionized base and then a second equivalent, the heat-effects for the two equivalents of base are usually different; for example, at 18° the two heat-effects are 14,600 and 16,600 cal. in neutralizing 0.28 normal sulfuric acid solution with 0.28 normal sodium hydroxide solution, and they are 11,100 and 9,100 cal. in neutralizing carbonic acid with that base.

(5) When certain polybasic acids are neutralized, there is sometimes scarcely any heat-effect when the second or third equivalent of base is added. Thus the successive heat-effects when phosphorous acid ( $\text{H}_3\text{PO}_3$ ) is treated with sodium hydroxide at 18° are: 14,800 cal. with the first equivalent, 13,600 cal. with the second equivalent, and only 500 cal. with the third equivalent; and with hypophosphorous acid ( $\text{H}_3\text{PO}_2$ ) there is a heat-effect of 15,200 cal. with the first equivalent of sodium hydroxide, and only 110 cal. with the second equivalent.

(6) With certain polybasic acids there is a considerable heat-effect when to the solution of the neutral salt another equivalent of base is added; thus, there is a heat-effect of 1200 cal. on mixing a solution containing one equivalent of sodium hydroxide with one containing one formula-weight of sodium phosphate ( $\text{Na}_3\text{PO}_4$ ).

*Interpretation of the Heats of Reaction in Aqueous Solutions.*—

*Prob. 20.* — *a.* Explain principle (1) stated in the preceding text with the aid of the ionic theory, assuming that the solutions are very dilute. *b.* What conclusion as to the ionization or as to the heat of ionization of neutral salts can be drawn from the fact that this principle holds true even at fairly high concentrations (such as 0.3 normal)? *c.* Write a thermochemical equation corresponding to the ionic reaction to which the heat-effect is mainly due in the reaction cited as an exception to the principle.

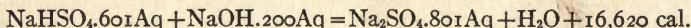
*Prob. 21.* — Show that on mixing dilute solutions of two salts (such as lead nitrate and potassium iodide) which form a precipitate by metathesis there must be a heat-effect which is substantially equal, but opposite in sign, to the heat of solution of the precipitated substance (the lead iodide).

*Prob. 22.* — *a.* Write the ionic reaction to which the nearly constant heat of neutralization of largely ionized acids and bases corresponds. *b.* State what other heat-effect is involved in the neutralization of ammonium hydroxide (a slightly ionized base) with a largely ionized acid, and find its value. *c.* What is the heat-effect that attends the reaction between 1NH<sub>4</sub>Cl and 1NaOH in 0.2 normal solution?

*Prob. 23.* — Calculate the heat of ionization of 1HF from the facts that its heat of neutralization in 0.28 normal solution with 0.28 normal NaOH solution has been found to be 16,300 cal., and its ionization in 0.28 normal solution is estimated to be 5.2%.

*Prob. 24.* — Calculate the heats of ionization at 18°, *a.* of H<sub>2</sub>CO<sub>3</sub>, and *b.* of HCO<sub>3</sub><sup>-</sup> from the heats of neutralization of carbonic acid given in paragraph (4). Carbonic acid is a very slightly ionized acid; sodium hydrogen carbonate solution is practically neutral; and the sodium carbonate in the 0.07 formal solution produced by the neutralization is 6.3% hydrolyzed.

*Prob. 25.* — Conductance, transference, and reaction-rate measurements have shown that sodium hydrogen sulfate in 0.1 formal solution at 18° consists approximately of 52% of HSO<sub>4</sub><sup>-</sup>, 48% of SO<sub>4</sub><sup>=</sup>, and of the corresponding amounts of Na<sup>+</sup> and H<sup>+</sup>. A calorimetric measurement at 18° has given the result expressed by the equation:



Calculate the heat of the reaction  $\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{=}$ , assuming that the ionization of NaOH, of Na<sub>2</sub>SO<sub>4</sub>, and of NaHSO<sub>4</sub> (into Na<sup>+</sup> and HSO<sub>4</sub><sup>-</sup>) is complete.

*Prob. 26.* — State what the observed heat-effects, given in paragraph (5), attending the neutralization of phosphorous acid and of hypophosphorous acid show as to the existence of salts of these acids in solution.

*Prob. 27.* — Explain the fact, stated in paragraph (6), that there is a large heat-effect on adding a solution of NaOH to one of Na<sub>3</sub>PO<sub>4</sub>.

*Prob. 28. — Determination of Chemical Equilibria by Thermochemical Methods.* — Describe a thermochemical method of determining the extent to which acetic acid displaces hydrofluoric acid from sodium fluoride in dilute solution. The heat of neutralization of acetic acid with sodium hydroxide at  $18^\circ$  is 13,230 cal., and that of hydrofluoric acid is 16,300 cal.

**\*134. Applications of Thermochemical Principles.** — The following problems illustrate some important applications of thermochemical principles to industrial chemical operations. Thus the problems include the estimation of the maximum temperature produced by flames or by the explosion of gaseous mixtures, the determination of the quantity of heat produced in continuous chemical processes (whose removal often constitutes one of the main difficulties of large-scale operation), and a consideration of the effectiveness of hot gases as an evaporating agent.

*Maximum Temperature Producible by Flames and Explosions.* —

*Prob. 29.* — Calculate the maximum temperature that could theoretically be attained in the flame produced by burning at  $20^\circ$  a "water-gas" consisting of equimolal quantities of hydrogen and carbon monoxide with twice the quantity of air required for complete combustion. Assume that the reaction-products are not appreciably dissociated, and that air contains  $1\text{O}_2$  to  $4\text{N}_2$ . The molal heat-capacity of  $\text{CO}_2$  at constant pressure at  $T$  is  $7.0 + 0.0071T - 0.000,001,86T^2$ . The equation  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{H}_2\text{O}(\text{l}) + 68,400 \text{ cal.}$  holds true at  $20^\circ$ . For the other data needed see Art. 27 and previous problems of this chapter.

*Ans.*  $1723^\circ\text{A.}$

*Prob. 30.—a.* Calculate the maximum temperature and pressure that could be produced by the explosion within a bomb of a mixture consisting of 1 mol of  $\text{H}_2$ ,  $\frac{1}{2}$  mol of  $\text{O}_2$ , and 1 mol of  $\text{N}_2$  at  $20^\circ$  and 100 mm., assuming that the water produced is not appreciably dissociated. *b.* The maximum pressure produced in an actual experiment was found to be 840 mm. Show how from this result the degree of dissociation of the water-vapor and the temperature of the mixture at the moment of the explosion can be calculated. (The equations should be formulated, but they need not be solved numerically.)

*Heat Evolved by Continuous Processes at High Temperatures.* —

*Prob. 31.* — In the Deacon process of making chlorine, a mixture of oxygen and hydrogen chloride in the proportion  $\frac{1}{2}\text{O}_2 : 1\text{HCl}$  at  $20^\circ$  is passed continuously into a vessel at  $386^\circ$  containing a suitable catalyzer. The gas is passed so slowly that equilibrium is established, 80% of the hydrogen chloride being converted into chlorine and water. Calculate the heat which will be given off from the equilibrium vessel per mol of  $\text{HCl}$  passed through, and which must, to maintain a constant

temperature, be continuously withdrawn by a suitable system of cooling. For the data needed see Art. 27 and previous problems of this chapter. *Ans.* 1900 cal.

*Prob. 32.* — In the Grillo contact process of making fuming sulfuric acid a mixture of sulfur dioxide and air passes through a chamber containing a series of trays charged with the platinum catalyst. This mixture enters the chamber at  $380^{\circ}$  (the lowest temperature at which a rapid reaction will occur), and rises in temperature as a result of the heat of reaction. This rise in temperature must not exceed  $100^{\circ}$ , if considerable dissociation of the  $\text{SO}_3$  is to be avoided. Calculate the smallest volume of air that may be present with one volume of sulfur dioxide in the gas entering the chamber at  $380^{\circ}$  in order that the rise of temperature may not exceed  $100^{\circ}$ . The heat-effect of the reaction  $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) = \text{SO}_3(\text{g})$  is 22,000 cal. at  $380^{\circ}$ . Consider the molal heat-capacity of each gas in the mixture to be the same as that of nitrogen or oxygen. Assume that 97% of the  $\text{SO}_2$  is converted into  $\text{SO}_3$ , and that there is no loss of heat by heat interchange. *Ans.* 29 volumes.

*Prob. 33. — Heat-Effects in the Process of Concentrating Sulfuric Acid by Hot Gases.* — In the Gaillard process of concentrating sulfuric acid a 73% acid (corresponding to  $1\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ ) is sprayed at  $20^{\circ}$  into a brick-lined tower, and in falling through the tower is caused to meet an ascending current of hot producer-gas consisting (mainly) of nitrogen and carbon monoxide, which enters the bottom of the tower at  $1100^{\circ}$  and leaves the top at  $200^{\circ}$ . Calculate how many cubic meters of producer gas must be supplied per kilogram of the 73% acid to furnish the heat necessary to concentrate it to 91½%  $\text{H}_2\text{SO}_4$  (corresponding to  $2\text{H}_2\text{SO}_4 \cdot 1\text{H}_2\text{O}$ ), assuming the latter leaves the tower at  $200^{\circ}$ , and that there is no loss of heat by radiation. The heat evolved on adding  $\text{NH}_2\text{O}(\text{l})$  to  $1\text{H}_2\text{SO}_4(\text{l})$  at  $20^{\circ}$  has been calorimetrically determined and found to be expressed by the equation  $Q = 17860N/(N + 1.80)$ . The heat of vaporization of 1 g. of water at  $100^{\circ}$  is -537 calories. The mean specific heat-capacity of 91½%  $\text{H}_2\text{SO}_4$  between  $20^{\circ}$  and  $200^{\circ}$  is 0.4 cal. per degree. In solving this problem write the thermochemical equations by which  $1\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$  at  $20^{\circ}$  can be converted into  $1\text{H}_2\text{SO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  and  $1\frac{1}{2}\text{H}_2\text{O}(\text{g})$  at  $200^{\circ}$ . *Ans.* 3.9.

## CHAPTER X

### THE PRODUCTION OF WORK BY ISOTHERMAL CHEMICAL CHANGES IN RELATION TO THEIR EQUILIBRIUM CONDITIONS

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#### I. THE SECOND LAW OF THERMODYNAMICS AND THE CONCEPT OF FREE-ENERGY

**135. The Second Law of Thermodynamics and its Application to Isothermal Changes in State.** — This chapter is devoted to a consideration of the production of work by chemical changes. Before this can be adequately considered, familiarity with certain aspects of another general principle relating to energy, the so-called second law of thermodynamics, is essential.

The first law of thermodynamics states that when one form of energy is converted into another the quantity of the form of energy that is produced is equivalent to the quantity of the form that disappears; but it does not indicate that there is any other restriction as to the transformability of the different forms of energy. Experience has shown, however, that while the various forms of work can be completely transformed into one another and into heat, the transformation of heat into work is subject to certain limitations. Namely, it is found that heat is never transformed into work by any cycle of changes taking place in any system kept in surroundings at any definite temperature; by a *cycle of changes* being meant any series of changes in state of such a character that the system finally returns to its initial state.

If a cycle of changes in state by which heat is transformed into work at constant temperature could be realized, the cycle could be indefinitely repeated and produce work in unlimited quantity, thus constituting a form of perpetual motion, which may be called *perpetual motion of the second kind*. The impossibility of such perpetual motion is the principle that was stated and illustrated in Art. 44.

Perpetual motion of the second kind, by which work is conceived to be produced out of heat at constant temperature, is to be distinguished from perpetual motion of the first kind (described in Art. 23), by which work is conceived to be produced without consuming energy of any form.

Experience with processes taking place at different temperatures

has led to the conclusion that this principle is a consequence of a still more general law, known as the *second law of thermodynamics*, which may be expressed as follows. A process whose final result is only a transformation of a quantity of heat into work is an impossibility. The application of this law to changes of state taking place at constant temperature will be considered in this chapter; its application to processes involving different temperatures, in chapter XII.

*Prob. 1. — Production of Work from Heat at Constant Temperature. —*

When a gas that is placed in a reservoir of large heat-capacity and definite temperature expands against an external pressure, it produces work and withdraws from the reservoir a quantity of heat. State why this transformation of heat into work is not a contradiction of the second law of thermodynamics.

Volume changes

Since work is never produced out of heat by any isothermal cycle of changes in a system, no change in state at constant temperature can produce more work than must be expended to restore the system to its initial state. In other words, any isothermal change in state taking place in one direction (such as the expansion of a gas from  $p_1, v_1$ , to  $p_2, v_2$ , at  $T$ ) is capable of producing a definite maximum quantity of work; and to make it take place in the opposite direction (thus, to compress the gas from  $p_2, v_2$ , to  $p_1, v_1$ , at  $T$ ), there must be expended a quantity of work at least equal to this maximum. Whether this maximum work is actually produced, or whether no more than this minimum work is actually expended, depends on the way or process by which the change in state takes place. Thus, the work produced by the change in state of the gas from  $p_1, v_1$ , to  $p_2, v_2$ , at  $T$  depends on the process by which this takes place; for example, upon the opposing external pressure, which obviously may have any value from zero up to a value only infinitesimally less than the pressure of the gas itself. If the process is such that the maximum work is actually produced or only the minimum work is expended, it is called a reversible process. If the process is such that less than the maximum work is produced or more than the minimum work is expended, it is called an *irreversible process*. It will be noted that the criterion of the reversibility of a change in state is whether the system can be restored to its initial state without a net expenditure of work.

The following problems illustrate reversible and irreversible processes and the external conditions which must be fulfilled in order that processes may be reversible.

*Reversible and Irreversible Processes Contrasted. —*

*Prob. 2.* —  $N$  mols of a perfect gas having a pressure of 2 atm. are enclosed within a cylinder placed in a thermostat at a temperature  $T$  and provided with a weighted piston. The weight on the piston is reduced so that the piston exerts on the gas a pressure of 1 atm., and the gas expands till its own pressure becomes 1 atm. Explain why this process is irreversible; and state what would have to be true of the pressure exerted by the piston on the gas during its expansion in order that the process might be reversible.

*Prob. 3.* — *a.* Derive an expression in terms of  $N$ ,  $R$ , and  $T$  for the work produced by the irreversible process described in Prob. 2. *b.* Derive a corresponding expression for the work produced when the same change in state is brought about by a reversible process. *c.* Find the numerical ratio of these two quantities of work.

*Prob. 4.* — Two Daniell cells, each having an electromotive force of 1.10 volts, are connected in series and are used for charging a lead storage-cell having a (counter) electromotive force of 2.10 volts. Explain why the process is not reversible; and state how a number of Daniell cells and a number of storage-cells could be so arranged that the latter might be charged reversibly. (In this case the Daniell cells may be regarded as the system, and the storage cells as a part of the surroundings in which the electrical work is produced and stored.)

As illustrated by the preceding problems, in order that the process by which a change in state is brought about may be reversible, the pressure externally applied must be substantially equal to the pressure exerted by the system itself, or the applied electromotive force must be substantially equal to the electromotive force of the cell. For the change in state will take place in one direction when the applied pressure or electromotive force is only infinitesimally less than that of the system, and in the other direction when it is only infinitesimally greater, and correspondingly, the work produced by the change in state is only infinitesimally less than that expended in restoring the system to its initial state. But, if the applied pressure or electromotive force were less by a finite amount than that of the system, the quantity of mechanical or electrical work produced in the surroundings would evidently not suffice to restore the system to its initial state; and if in causing the change to take place in the opposite direction, the applied pressure or electromotive force were greater than that of the system, more work would be withdrawn from the surroundings than the system would be capable of reproducing on reverting to its original state.

It is to be noted that the term reversible is always employed, in

the sense above defined, to designate a process of such a character that it is possible to restore the original condition of things both in the system and its surroundings. After an irreversible process has taken place, it is in general possible to restore the system to its original state, but only by withdrawing from the surroundings a larger quantity of work than was produced in them (and imparting to them a corresponding quantity of heat), so that the original condition in the surroundings is not reproduced. When an irreversible change has once taken place, it is not possible by any means whatever to reproduce in their entirety the conditions that previously existed.

Since all actual processes are irreversible, there is constantly taking place a decrease in the work-producing power of the universe. This irreversibility arises from various causes. Thus there may be no device for producing the available work (as when a compressed gas escapes into the atmosphere or when coal burns in the open air); the mechanism that is employed may be imperfect owing to frictional or electrical resistance; or the pressure or electromotive force of the system may not be balanced by applying an equal and opposite external pressure or electromotive force.

**136. The Concepts of Work-Content and Free Energy.** — The principles that a definite change in state is capable of producing a definite quantity of work and that this quantity of work is realized when, and only when, the process by which the change is effected is reversible, are further illustrated by the following problem.

*Prob. 5. — Production of Definite Quantity of Work by Reversible Changes in State.* — In a voltaic cell consisting of one platinum electrode in contact with a 0.1 f. HCl solution and with hydrogen gas at 1 atm. and of a second platinum electrode in contact with the same HCl solution and with hydrogen gas at 0.1 atm., hydrogen is found to go into solution (as hydrogen-ion) at the first electrode and to be evolved at the second electrode, as a result of the electromotive force which is produced. *a.* Name the change in state that takes place in such a cell when one faraday of electricity passes through it at 18°, specifying all the factors determining the change in state, but disregarding the transference in the solution, which in a cell of this kind will be shown later to be attended by no energy-effect. *b.* Describe how the same change in state could be brought about reversibly by a process not involving voltaic action; and calculate the work attending this process. *c.* Show that perpetual motion could be realized if this quantity of work were not equal to the work that would be produced per faraday of electricity when the cell operates reversibly.

Since any definite change of state in a system is capable of producing a definite maximum quantity of work (a quantity which is never exceeded, whatever be the process by which the change in state takes place), it is to be inferred that a system in any definite state possesses a certain power of producing work, which may be called its work-content  $A$ ; and that this changes by some definite amount (from  $A_1$  to  $A_2$ ) when the system undergoes any definite change in state, whatever be the process by which this change takes place, and whatever be the quantity of work which is actually produced. In other words, the work-content of a system, like its energy-content and its heat-content, is a quantity characteristic of the state of the system; and the change in the work-content of a system is determined solely by its initial and final states.

The decrease ( $A_1 - A_2$  or  $-\Delta A$ ) in the work-content of the system attending a definite change in its state is evidently equal to the maximum work which the change is capable of producing, and this is equal to the quantity of work  $W_R$  which the change actually produces when it takes place reversibly. That is:

$$A_1 - A_2 = -\Delta A = W_R.$$

It will be noted that, while the First Law requires that there be a quantity of energy produced in the surroundings equal to the decrease of the energy-content of the system, the Second Law does not require that there be a quantity of work ( $W$ ) produced equal to the decrease in work-content (as was illustrated by Prob. 3). The Second Law requires only that the quantity of work produced be not greater than the decrease in work-content. That is,  $W > -\Delta A$  for no process whatever;  $W = -\Delta A$  for a reversible process; and  $W < -\Delta A$  for an irreversible one.

Just as it is more convenient in chemical considerations to consider the heat-content rather than the energy-content of systems, so there are many advantages in considering in place of the work-content a quantity which differs from it, just as the heat-content differs from the energy-content, by the value of the pressure-volume product. This quantity, which may be called the *free-energy content* ( $F$ ), or simply the *free-energy* of the system, is defined by the equation  $F = A + pv$ . Its value is determined by the state of the system, since the values of  $A$  and of  $pv$  are so determined; and the decrease in its value when any change in the state of the system takes place is evidently equal to the work produced when the change takes place reversibly,

diminished by the increase of the pressure-volume product; that is:

$$F_1 - F_2 = W_R - (p_2 v_2 - p_1 v_1), \text{ or } -\Delta F = W_R - \Delta(pv).$$

The difference  $(F_1 - F_2)$  between the free-energy-content of a system in its initial state and that in its final state will be called the free-energy decrease  $(-\Delta F)$  attending the change in state, irrespective of the sign of its numerical value, which may be either positive or negative. The change in state is always considered to take place at some constant temperature.

*Prob. 6. — Work-Content and Free-Energy-Content in Relation to the Work Produced. — a.* What is the decrease in joules in the energy-content, heat-content, work-content, and free-energy-content of one formula-weight of water when it changes from liquid water to gaseous water at  $100^\circ$  against a constant pressure of 1 atm., referring to Prob. 38, Art. 23, for the data needed? *b.* What would be the decrease in these four quantities if the liquid water at  $100^\circ$  and 1 atm. changed to gaseous water at  $100^\circ$  and 1 atm. by a process which produces no work, for example, by introducing the liquid water into an evacuated vessel having a volume equal to that of the saturated vapor?


In cases where different parts of the system are under different pressures, as in the cell of Prob. 5, the decrease in free energy is defined to be the quantity obtained by subtracting from the work produced when the change takes place reversibly the difference between the sum of the  $p v$  values for all the parts of the system in its final state and the sum of the  $p v$  values for all its parts in its initial state. Therefore, in general:

$$F_1 - F_2 = W_R - (\Sigma p_2 v_2 - \Sigma p_1 v_1); \text{ or } -\Delta F = W_R - \Delta(\Sigma p v).$$

The principle that the free-energy decrease attending any process is determined solely by the change in state of the system is the fundamental principle on which is based the treatment of chemical equilibrium and of electrochemical processes presented in this and the following chapters. The methods of determining the free-energy change attending various kinds of changes in state will be systematically developed, and the applications of the results to chemical and electrochemical problems will be considered.

A knowledge of the free-energy changes attending chemical changes is of great importance for the following reasons. In the first place, free energy values give directly the maximum quantity of work obtainable from chemical changes; for example, they show how much work can be produced by the combustion of coal or gasoline or from the chemical

reactions taking place in a storage cell; for the decrease in free-energy attending the chemical change, and not its heat-effect, determines the theoretical efficiency of a heat engine or electric battery. Secondly, free-energy values enable the equilibrium-constants of chemical reactions to be calculated; and a knowledge of the equilibrium conditions of chemical changes is fundamental both in its scientific aspects and in its technical applications; thus the proper control of a gas producer or of a blast furnace must be based on a quantitative consideration of the equilibria of the chemical reactions involved in the process. Thirdly, free-energy values form the basis of the science of electrochemistry on the electromotive force side; thus they enable not only the total electromotive force, but also the separate potentials, of voltaic cells of all kinds to be calculated.



## II. FREE-ENERGY CHANGES ATTENDING PHYSICAL CHANGES

**137. Free-Energy Changes Attending Changes in Volume and Pressure.** — In finding the expression for the free-energy decrease attending any kind of change in state, the method of procedure is always as follows. First, the change in state of the system is formulated by defining accurately its initial and final states; second, a process is conceived by which the change in state takes place reversibly; and third, the work attending this reversible process is evaluated.

The simplest type of change in state is that in which a system whose pressure is  $p$  and volume  $v$  changes its state at a constant temperature  $T$  so that its pressure becomes  $p + dp$  and its volume  $v + dv$ . This change in state will take place reversibly if a substantially equal external pressure be applied to the system. The work  $dW_R$  in this process is equal to  $p dv$  (Art. 24). The free-energy decrease  $-dF$  attending such a change in state at a constant temperature is, however, by definition equal to  $dW_R - d(pv)$ . In virtue of the mathematical relation  $d(pv) = p dv + v dp$ , the free-energy decrease attending an infinitesimal change in volume or pressure at a constant temperature is therefore given by the expression:

$$-dF = -v dp.$$

For a finite change in volume or pressure the corresponding expression is:

$$-\Delta F = \int_{p_1}^{p_2} v dp.$$

This equation is a general one, applicable to gaseous, liquid, and solid systems. In order to carry out the indicated integration, the functional relation between the pressure and volume of the system at constant temperature must be known.

*Prob. 7. — Free-Energy Decrease Attending the Expansion of Gases. —*

*a.* Derive an expression for the free-energy decrease attending the change in state of  $N$  mols of a perfect gas when at the temperature  $T$  its volume and pressure change from  $v_1$  and  $p_1$  to  $v_2$  and  $p_2$ . *b.* Derive by integration an expression for the decrease of the free energy of  $N$  mols of a gas when at  $T$  its pressure changes from  $p_1$  to  $p_2$ , provided the pressures are moderate so that its pressure-volume relations are expressed with sufficient accuracy by the equation  $p v = NRT(1 + \alpha p)$  given in Art. 15. *c.* Calculate by this expression the value in joules of the free-energy decrease attending the expansion of 1 mol of  $\text{CO}_2$  from 4 atm. to 1 atm. at  $0^\circ$ , for which substance at  $0^\circ$  the deviation-coefficient  $\alpha$  has the value  $-0.0068$  per atmosphere. *Ans. c, 3100.*

*\*Prob. 8. — Free-Energy Decrease Attending the Compression of Liquids.* — The change in volume  $v$  of liquid or solid substances with the pressure  $p$  can commonly be approximately expressed by the equation  $v = v_0(1 - kp)$ , where  $v_0$  is the volume at zero pressure and  $k$  is a quantity, called the *compression-coefficient*, which varies with the substance and with the temperature, but may ordinarily be regarded as constant for variations of pressure up to 30 to 50 atm. *a.* Derive an expression for the decrease in free energy of such a substance when the pressure on it changes from  $p_1$  to  $p_2$ . *b.* Find the free-energy decrease in joules attending the compression from 1 atm. to 50 atm. at  $20^\circ$  of 10 g. of water, whose compression-coefficient at  $20^\circ$  is 0.000048 when the pressure is in atmospheres, and whose density at  $20^\circ$  and 1 atm. is 0.998. *Ans. b,* 49.7.

**138. Free-Energy Changes Attending the Transfer of Substances between Solutions of Different Concentrations.** — As shown in the problems below, there may readily be derived the following expressions for the free-energy decrease which attends the transfer at the temperature  $T$  of that quantity of a substance which is  $N$  mols in the state of a perfect gas from an infinite quantity of a solution in which its vapor-pressure is  $p_1$ , its mol-fraction  $x_1$ , and its molality or molal concentration  $c_1$ , into an infinite quantity of another solution in which its vapor-pressure is  $p_2$ , its mol-fraction  $x_2$ , and its molality or molal concentration  $c_2$ :

$$-\Delta F = NRT \ln \frac{p_1}{p_2} \quad (1)$$

$$-\Delta F = NRT \ln \frac{x_1}{x_2} \quad (2)$$

$$\left[ -\Delta F = NRT \ln \frac{c_1}{c_2} \right] \quad (3)$$

The conditions under which each of these equations is exact will be evident from its derivation. Equation (1) holds true whatever be the mol-fractions or concentrations; but it involves the assumption that the vapor conforms to the perfect-gas law. Equation (2) holds true when, in conformity either with Raoult's law or with Henry's law, the vapor-pressures are proportional to the mol-fractions. Equation (3) holds true when, in conformity with Henry's law, the vapor-pressures are proportional to the mol-fractions and when the latter are small enough to be substantially proportional to the concentrations; it is the expression commonly employed when a solute is transferred from one dilute solution to another.

*Derivation of the Free-Energy Equations. —*

*Prob. 9. — a.* Formulate an exact expression (not involving the perfect-gas law) for the free-energy decrease attending the introduction at the temperature  $T$  of  $m$  grams of a pure substance at a pressure equal to its vapor-pressure  $p_0$  into an infinite quantity of a solution in which the substance has a vapor-pressure  $p$ . Note that this change in state can be brought about by the following reversible process: vaporize the  $m$  grams of the substance at the temperature  $T$  under a pressure  $p_0$ ; change the pressure of this vapor to  $p$ ; and at this pressure condense the vapor into the solution. *b.* Derive from this expression an equation which holds true when the vapor conforms to the perfect-gas law. *c.* Formulate an expression for the free-energy decrease attending the transfer of  $N$  mols of a substance from an infinite quantity of a solution in which its vapor-pressure is  $p_1$  into an infinite quantity of a solution in which its vapor-pressure is  $p_2$ .

*Prob. 10. —* Show how the equation formulated in Prob. 9c may be modified so as to contain the mol-fractions  $x_1$  and  $x_2$  of the substance in the two solutions, *a*, when the vapor-pressures  $p_1$  and  $p_2$  conform to Raoult's law; *b*, when these vapor-pressures conform to Henry's law. *c.* State in the case of a solution consisting of two substances A and B the conditions of composition under which Raoult's law and under which Henry's law (and therefore under which the corresponding free-energy expressions) hold true approximately. *d.* Show that when the mol-fractions  $x_1$  and  $x_2$  are small, their ratio may be replaced by the ratio of the molalities or molal concentrations, which signify (Art. 35) the number of mols of the solute per 1000 grams or 1000 ccm., respectively, of the solvent.

Since Henry's law applies to the concentrations of a definite chemical substance, it is evident that equation (3) must be applied separately to the transfer of each chemical substance, not to the transfer of the substance as a whole, if it exists in the solution as two or more different chemical substances as is the case with  $\text{H}^+\text{Cl}^-$  or any other partially ionized substance in aqueous solution, or with acetic acid in benzene solution in which it exists as  $\text{C}_2\text{H}_4\text{O}_2$  and  $(\text{C}_2\text{H}_4\text{O}_2)_2$ .

Although equation (3) was derived by the consideration of a process involving the vaporization of the solute and with the aid of the assumption that the pressure of the vapor was small enough to conform to the perfect-gas law, yet that equation relates only to the transfer of the substance from one solution to another; and it would be remarkable if its validity depended on whether the substance were volatile or on how large its vapor-pressure might be. In fact, it can be shown, by deriving equation (3) through a consideration of an osmotic process of transferring the substance from one solution to the

other, that the equation is exact, provided only that the substance behaves as a perfect solute, as shown by its conformity to the osmotic-pressure equation  $Pv_0 = NRT$  considered in Art. 52.

*Applications of the Free Energy Equations. —*

*Prob. 11. — a.* Calculate the free-energy decrease attending the transfer at  $20^\circ$  of  $1\text{NH}_3$  from an infinite quantity of a solution of the composition  $1\text{NH}_3.8\frac{1}{2}\text{H}_2\text{O}$  in which its vapor-pressure is 80 mm. into an infinite quantity of a solution of the composition  $1\text{NH}_3.21\text{H}_2\text{O}$  in which its vapor-pressure is 27 mm. *b.* Calculate the free-energy decrease attending the dissolving at  $20^\circ$  of  $1\text{NH}_3$  at 1 atm. in an infinite quantity of a solution of the composition  $1\text{NH}_3.21\text{H}_2\text{O}$ .

*Note. —* Throughout this chapter free-energy values are to be expressed in calories.

*Prob. 12. —* Calculate the free-energy decrease attending the transfer at  $20^\circ$  of  $1\text{NH}_3$  from an infinite quantity of 0.1 formal  $\text{NH}_4\text{OH}$  solution into an infinite quantity of 0.001 formal  $\text{NH}_4\text{OH}$  solution. The ammonium hydroxide is 1.3% ionized in the 0.1 formal and 12.5% ionized in the 0.001 formal solution, and the remaining ammonium hydroxide is  $y$  per cent dissociated into  $\text{NH}_3$  and  $\text{H}_2\text{O}$  in each solution.

*Prob. 13. —* The transfer at the temperature  $T$  of one formula-weight of  $\text{HCO}_2\text{H}$  from an infinite quantity of a dilute solution in which its formality is  $c_1$  and its ionization is  $\gamma_1$  into an infinite quantity of another dilute solution in which its formality is  $c_2$  and its ionization is  $\gamma_2$  can be brought about by so transferring either 1 mol of  $\text{HCO}_2\text{H}$  or one mol of  $\text{H}^+$  and one mol of  $\text{HCO}_2^-$ . *a.* Formulate an expression for the free-energy decrease attending each of these processes. *b.* Show that one of these expressions can be derived from the other with the aid of the mass-action equation for the ionization of the salt. *c.* Calculate the free-energy decrease by both expressions for the case that the temperature is  $25^\circ$ , the concentrations are 0.1 and 0.001 formal, and the ionizations are 0.045 and 0.360.

*Prob. 14. —* Formulate an expression for the free-energy decrease attending the transfer of  $1\text{K}_2\text{SO}_4$  at  $25^\circ$  from a 0.1 formal solution to a 0.001 formal solution, assuming that the salt is completely ionized and that the ions act as perfect solutes.

*Note. —* The assumptions that largely ionized substances are completely ionized and that their ions are perfect solutes are to be made, unless otherwise stated, also in all later problems.

\*Owing to the fact that ions at even small concentrations are imperfect solutes, the free-energy decrease attending the transfer of largely ionized substances is expressed only as a rough approximation by equation (3). An expression exact at any concentration may, however, be formulated with the aid of the concept of activity presented in Art. 113. Namely, it follows from the proportionality

between the activity of any definite substance in a solution and its vapor-pressure (assuming the vapor to be a perfect-gas) that the ratio of the activities of a substance in two solutions, or in general in two phases, may be substituted for the ratio of the pressures in equation (1). Hence, for the transfer of  $N$  mols of a chemical substance at  $T$  from a solution or phase in which its activity is  $a_1$  to a solution or phase in which its activity is  $a_2$  the free-energy decrease is:

$$-\Delta F = NRT \log \frac{a_1}{a_2}. \quad (4)$$

\*This equation has practical significance, not so much because it furnishes a means of evaluating free energies, as because it supplements the primary definition of activity (given by the equation  $a_1/a_2 = p_1/p_2$ ) by a secondary definition which affords another method of determining the relative activities of a substance in different solutions. Namely, it enables activities and activity-coefficients to be derived from the free-energy decrease attending the transfer of the substance in cases where this decrease can be obtained from other measurements than those of vapor-pressure. It will be shown in Art. 146 that this decrease can be computed from the electromotive force of certain types of voltaic cells; and applications of equation (4) will there be considered.

**139. Free-Energy Changes Attending the Transfer of Substances between Different Phases.** — When the change in state consists in the transfer of a substance from one phase to another phase at the temperature and pressure at which the two phases are in equilibrium, the free-energy decrease is zero. Changes in state of this type are the transition, fusion, or vaporization of a solid substance, and the freezing or vaporization of a liquid substance, provided the two phases are at the temperature and pressure at which they are in equilibrium. This principle follows from the general expression for free-energy decrease,  $-\Delta F = W_R - \Delta(pv)$ , and from the fact that this type of change can be made to take place reversibly at the given pressure, so that the maximum work  $W_R$  is simply equal to that pressure times the volume-increase, that is, to  $p(v_2 - v_1)$ , which is identical with  $\Delta(pv)$ .

*Prob. 15. — Vaporization, Fusion, and Transition in Relation to Free Energy.* — Name a condition of temperature and pressure at which the free energies are equal and a condition under which they are not equal,  $a$ , for water as a liquid and as a gaseous phase;  $b$ , for water as a solid and as a liquid phase;  $c$ , for sulfur in the rhombic and the monoclinic forms (see Art. 115).

Another case of this type is the transfer of a substance from a solid phase to a solution saturated with respect to that substance at a definite temperature and pressure. In order that this change in state may take place reversibly, the solid substance is made to dissolve in an infinite volume of its saturated solution by increasing or decreasing the pressure on the two phases by an infinitesimal amount. The work produced in this process is again simply equal to the pressure times the change in volume ( $p \Delta v$ ), and the free-energy decrease is therefore zero.

*Prob. 16. — Solution in Relation to Free Energy.* — Find the maximum work and the free-energy decrease attending the melting of  $1\text{H}_2\text{O}$  as ice at  $-1.69^\circ$  into a 0.5 formal NaCl solution at its freezing-point  $-1.69^\circ$  at 1 atm. The molal volume of ice is 19.6 ccm., and the increase in volume of an infinite quantity of the solution when  $1\text{H}_2\text{O}$  is added to it is 18.0 ccm.

Still another case of this type is the transfer at a definite temperature of a substance from one liquid phase to another liquid phase, thus from a solution of it in one solvent to a solution of it in another solvent not miscible with the first solvent. Provided the substance is present in the two phases at the equilibrium concentrations, the free-energy decrease attending such a transfer is zero, as shown in Prob. 17.

*Prob. 17. — Distribution in Relation to Free Energy.* — A  $c_1$  formal solution of  $\text{NH}_3$  in chloroform is in equilibrium with a  $c_2$  formal solution of  $\text{NH}_3$  in water at  $T$ . Show that the free-energy decrease is zero for the transfer of  $1\text{NH}_3$  from an infinite quantity of the chloroform solution into an infinite quantity of the water solution, by considering a reversible process involving the vapor phase.

When the substance in one phase at any definite temperature is not in equilibrium with the same substance in the other phase, the transfer of it from one phase to the other is attended by an increase or decrease in its free-energy. In determining this free-energy change, a process must as usual be conceived by which the transfer takes place reversibly, and the work attending this reversible process must then be evaluated. This is illustrated by the following problems.

*Free-Energy Decrease Attending the Conversion of Unstable into Stable Phases.* —

*Prob. 18.* — Find the free-energy decrease that attends the transition at  $105^\circ$  of  $1\text{S}$  from the rhombic into the monoclinic form, each being at a pressure equal to its vapor-pressure, referring to the figure of Art. 115 for the data needed and assuming that the molecular formula of the sulfur vapor is  $\text{S}_8$ .

*Prob. 19.* — Find the free-energy decrease attending the transition of 32.06 g. of monoclinic to rhombic sulfur at  $25^\circ$  from the facts that at  $25^\circ$  the solubility in benzene of the monoclinic form is 23.2 g. and that of the rhombic form is 18.2 g. per liter of benzene, and that the molecular formula of sulfur in benzene has been shown by molecular-weight determinations to be  $S_8$ . Consider a reversible process that involves dissolving the monoclinic form in its saturated solution, transferring the sulfur from this solution to one saturated with respect to the rhombic form, and causing the rhombic form to precipitate. *Ans.* 18 cal.

*\*Prob. 20.* — *a.* Find the free-energy decrease that attends the change of  $H_2O$  from the state of liquid at  $-1^\circ$  and 4.255 mm. (its vapor-pressure at  $-1^\circ$ ) to the state of ice at  $-1^\circ$  and 4.215 mm. (its vapor-pressure at  $-1^\circ$ ) by considering a reversible process similar to that of Prob. 9. *b.* Find the free-energy decrease attending the same change in state, by considering a reversible process in which the water and ice are brought into equilibrium at  $-1^\circ$  by compression. Ice melts at  $-1^\circ$  when the pressure is 130 atm. The mean compression-coefficient (see Prob. 8) at  $0^\circ$  between zero pressure and this pressure is 0.000051 for water and 0.000034 for ice.

The foregoing considerations may be summed up in the following statements:

(1) The free energies of a substance in two different phases at any definite temperature are equal when the pressure or concentration is that at which there is equilibrium.

(2) When the pressure or concentration is not that corresponding to equilibrium, the substance in the unstable state has the greater free energy; and namely, a free energy greater by the amount given by the expressions  $NRT \log(p_1/p_2)$  and  $NRT \log(s_1/s_2)$ , in which  $p_1$  and  $p_2$  represent the vapor-pressures of the substance in the unstable and stable states, respectively, and  $s_1$  and  $s_2$  represent its solubilities in any solvent in the unstable and stable states, respectively. This second principle evidently corresponds to the principles stated in Art. 115 that the unstable form of a substance has the greater vapor-pressure and the greater solubility in any solvent.

These principles show that equality of the free energies of a substance in two phases is a criterion of equilibrium; and that, when the free energies are not equal, a change tends to take place in that direction in which there is an actual decrease in the free-energy.

\*Since the activity of the substance in any two phases is by definition proportional to its vapor-pressure (Art. 113), it follows that the activity of a substance is the same in different phases which are in

equilibrium with one another. For example, when solid iodine is shaken with water and chloroform at 25° in a closed vessel till equilibrium is reached, the activity of the iodine is the same in the solid, the gaseous, and the two liquid phases. This is a fundamental principle which is often made use of in applications of the mass-action law. Thus in the mass-action expression  $(\text{HI})^2/(\text{H}_2\text{S})(\text{I}_2) = K$ , for the equilibrium of the reaction  $\text{H}_2\text{S} + \text{I}_2 = 2\text{HI} + \text{S(s)}$  in aqueous solution, the concentrations of the  $\text{H}_2\text{S}$  and  $\text{HI}$  can be replaced by their vapor-pressures, and that of the  $\text{I}_2$  can be replaced by its concentration in a chloroform phase in equilibrium with the aqueous solution. Such substitutions are useful, either when the substance is an imperfect solute in the aqueous solution, or when its pressure in the gas phase or its concentration in another solvent can be more easily or more accurately determined than its concentration in the aqueous solution.

\*In case there is not equilibrium it follows from the relation between free-energy decrease and activities derived in Art. 138 that the ratio of the activities of the substance in the two phases is given by the equation:

$$\log \frac{a_1}{a_2} = \frac{-\Delta F}{NRT}.$$

Qualitatively this signifies that the activity of a substance is greater in the unstable state; for this state always passes over into the stable state with a positive free-energy decrease.

## III. FREE-ENERGY CHANGES ATTENDING CHEMICAL CHANGES

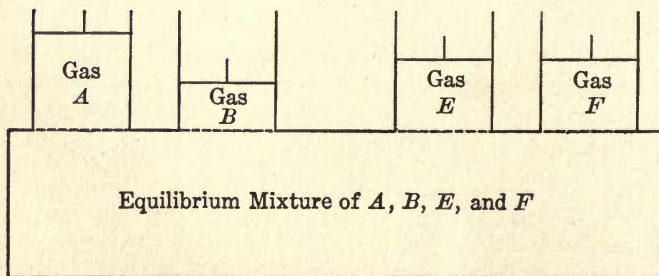
**140. The Free-Energy Equation for Chemical Changes between Perfect Gases.** — An expression for the free-energy decrease attending a chemical change between perfect gaseous substances in terms of the equilibrium-constant for that change can be derived by the following considerations.

Consider any chemical reaction  $aA + bB \dots = eE + fF \dots$  between the gaseous substances A, B, . . . E, F, . . . ; and consider a change in state which consists in the conversion at the temperature  $T$  of  $a$  mols of A,  $b$  mols of B, . . . at pressures  $p_A'$ ,  $p_B'$ , . . . into  $e$  mols of E and  $f$  mols of F, . . . at pressures  $p_E'$ ,  $p_F'$ , . . . This change in state is briefly expressed by the equation:

$$a A \text{ (at } p_A') + b B \text{ (at } p_B') \dots = e E \text{ (at } p_E') + f F \text{ (at } p_F') \dots$$

This reaction would take place continuously in one direction or the other (unless the pressures happened to be those corresponding to equilibrium) if infinite quantities of the gases, each at its specified pressure, were present together in a mixture; and the specified change in state would be realized if the period during which the specified number of mols reacted were considered. However, the change in state would not be taking place reversibly, since no mechanism is provided by which the work which the change is capable of producing would be actually produced. It is therefore necessary to conceive of some process by which the change in state can be made to take place reversibly. Such a process will now be described.

In the process an apparatus like that shown in the figure will be employed. This apparatus consists of a reservoir and of a number of cylinders which communicate with it through walls, each of which is permeable for only one of the gases. These walls can be replaced at will by impermeable ones. The cylinders, which serve to hold the



separate gases, are provided with weighted frictionless pistons. The reservoir contains a mixture of the gases at any partial pressures  $p_A, p_B, \dots p_E, p_F, \dots$  at which the chemical change is in equilibrium.

Starting now with  $a$  mols of A,  $b$  mols of B,  $\dots$  at pressures  $p_A', p_B', \dots$  in their respective cylinders, consider the following process to be carried out at the temperature  $T$  under reversible conditions, always keeping the external pressure on any piston equal within an infinitesimal amount to that of the gas beneath.

1. The cylinders being closed temporarily by impermeable walls, raise or lower the pistons above the gases A, B,  $\dots$  till the pressures change from  $p_A', p_B', \dots$  to those,  $p_A, p_B, \dots$ , prevailing in the equilibrium-mixture.

2. Replace the impermeable walls by semipermeable ones, and force the  $a$  mols of A,  $b$  mols of B,  $\dots$  into the reservoir, at the same time drawing out into the other cylinders at the pressures  $p_E, p_F, \dots$  prevailing in the equilibrium-mixture, the  $e$  mols of E,  $f$  mols of F,  $\dots$  which must form spontaneously out of A, B,  $\dots$  in order that the equilibrium in the mixture may be maintained.

3. Replace the semipermeable walls under the gases E, F,  $\dots$  by impermeable ones, and raise or lower the pistons above the gases E, F,  $\dots$  till the pressures change from the equilibrium-pressures  $p_E, p_F, \dots$  to the final pressures  $p_E', p_F', \dots$ .

By formulating, as is done in Prob. 21 expressions for the free-energy decrease attending each of the steps in this process and summing up the three values, there is obtained in the case that all the pressures involved are so small that they conform substantially to the perfect-gas law the following expression for the free-energy decrease attending an isothermal chemical change between gaseous substances:

$$-\Delta F = RT \left( \log \frac{p_E^e p_F^f \dots}{p_A^a p_B^b \dots} - \log \frac{p_E'^e p_F'^f \dots}{p_A'^a p_B'^b \dots} \right).$$

*Prob. 21. — Derivation and Significance of the Free-Energy Equation.*

*a.* Formulate expressions for the free-energy decrease attending each of the three steps in the process described in the preceding text. *b.* By combining these expressions derive the free-energy equation there given. *c.* State explicitly the change in state to which this equation applies and the difference in the significance of the pressures in the two logarithmic terms; and name a familiar quantity that may be substituted in one of these terms. *d.* Give the form which the equation assumes when the initial and final partial pressures are all unity.

*Prob. 22. — Evaluation of the Free-Energy Decrease.* — *a.* Calculate the free-energy decrease in calories attending at  $2000^{\circ}$  the change  $2\text{H}_2(0.1 \text{ atm.}) + \text{O}_2(0.5 \text{ atm.}) = 2\text{H}_2\text{O}(1 \text{ atm.})$  from the fact that water-vapor at  $2000^{\circ}$  and 1 atm. is 1.85% dissociated into hydrogen and oxygen. *b.* Calculate also the free-energy decrease at  $2000^{\circ}$  when the initial pressures of the hydrogen and the oxygen (as well as the final pressure of the water-vapor) are each 1 atm. *Ans. b, 57,120.*

*Prob. 23. — Derivation of the Mass-Action Law.* — Derive the mass-action law expressed in terms of pressures by considering in the derivation of the free-energy equation that the same change in state is brought about by two reversible processes of the type described in the text differing in the respect that different equilibrium mixtures are contained in the reservoir.

*Prob. 24. — Relation of the Free-Energy Change to the Tendency of the Chemical Change to Take Place.* — *a.* Show by the mass-action law that, when the pressures of the substances in a gaseous mixture are such that the free-energy decrease attending the reaction as computed by the free-energy equation has a positive value, the reaction as written takes place spontaneously from left to right; and that, when the pressures are such that the computed free-energy decrease has a negative value, the reaction as written takes place spontaneously from right to left; and therefore that the reaction always takes place in that direction in which there is a positive free-energy decrease. *b.* Show that equilibrium prevails when the pressures of the substances in a gaseous mixture are such that the computed free-energy decrease is zero.

The conclusions reached in the preceding problem afford another example of the following general principles, already shown in Art. 139 to apply to the transfer of substances between phases:

(1) When at any definite temperature the pressures or concentrations of the substances present in a system are such that a change in the state would be attended by zero change in free-energy, the substances involved in that change are in equilibrium with each other. That is, the condition  $-\Delta F = 0$  is a criterion of the equilibrium of the substances involved in any change in state.

(2) When at any definite temperature the pressures or concentrations are such that a change in the state of the system would be attended by a change in its free-energy, the change tends to take place in that direction in which the free-energy actually decreases. That is, a system can spontaneously change its state only in that direction for which  $-\Delta F$  is positive.

**141. The Free-Energy Equation for Chemical Changes between Perfect Solutes.** — It can be shown, as is done in Prob. 25, that the

free-energy decrease attending at the temperature  $T$  the chemical change:

$$aA(\text{at } c_A') + bB(\text{at } c_B') \dots = eE(\text{at } c_E') + fF(\text{at } c_F') \dots,$$

where  $A, B, \dots, E, F, \dots$  are dissolved substances at the concentrations  $c_A', c_B', \dots, c_E', c_F', \dots$ , which are so small that the substances behave as perfect solutes, is given by the equation:

$$-\Delta F = RT \left( \log \frac{c_E^e c_F^f \dots}{c_A^a c_B^b \dots} - \log \frac{c_E'^e c_F'^f \dots}{c_A'^a c_B'^b \dots} \right).$$

In this equation, which is obviously closely analogous to that for gaseous substances, the quantities  $c_A, c_B, \dots, c_E, c_F, \dots$  are any small concentrations at which the substances are in equilibrium.

*Prob. 25. — Derivation of the Free-Energy Equation.* — Derive the free-energy equation given in the preceding text by considering that all the solutes are volatile and that the change in state is brought about by vaporizing  $A, B, \dots$  out of their solutions, converting them into  $E, F, \dots$  in the gaseous state by the process described in the text of Art. 140, and condensing  $E, F, \dots$  into their solutions; each of these changes being carried out under equilibrium-conditions so that it may be reversible. Represent by  $p_A', p_A, \dots, p_E', p_E, \dots$  the partial vapor-pressures corresponding to the concentrations  $c_A', c_A, \dots, c_E', c_E, \dots$ , and assume that in accordance with Henry's law the pressures and concentrations are proportional.

*Prob. 26. — Evaluation of the Free-Energy Decrease.* — Calculate the free-energy decrease that attends at  $25^\circ$  the chemical change  $\text{NH}_4^+(\text{at } 0.1 \text{ f.}) + \text{CN}^-(\text{at } 0.1 \text{ f.}) = \text{NH}_3(\text{at } 0.1 \text{ f.}) + \text{HCN}(\text{at } 0.1 \text{ f.})$ , assuming that  $\text{NH}_4\text{CN}$  in  $0.1$  formal solution at  $25^\circ$  is 47% dissociated into  $\text{NH}_3$  and  $\text{HCN}$ , and that the remainder of the salt is completely ionized.

Although this free-energy equation was derived above under the assumptions that the solutes are volatile and that their concentrations and vapor-pressures are so small that Henry's law is applicable, it can be shown that this equation (like equation (3) of Art. 138) is valid provided only that the concentrations are so small that the solutes conform to the laws of perfect solutions.

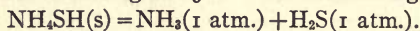
The mass-action law for perfect solutes can be derived from this free-energy equation just as the mass-action law for perfect gases was derived in Prob. 23 from the free-energy equation of the preceding article. The validity of the mass-action law therefore involves only that of the laws of perfect solutions or of perfect gases; and it will hold true when applied to any definite chemical change with a degree of

exactness corresponding to that with which the substances involved conform under the given conditions of concentration or pressure to the laws of perfect solutions or of perfect gases.

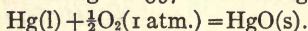
**142. The Free-Energy Equations for Chemical Changes between Solid Substances and Perfect Gases or Perfect Solutes.** — When pure solid substances are involved in a chemical change with gaseous or dissolved substances it is not necessary to include in the free-energy equation their pressures or concentrations; for these would obviously have the same value (that of the vapor-pressure or solubility of the solid) in the two logarithmic terms corresponding to the equilibrium conditions and to the initial and final conditions. The same is true of the pressure of a pure liquid when it is involved in a chemical change with gaseous substances that are not much soluble in it, as in the formation of liquid water from hydrogen and oxygen.

*Evaluation of the Free-Energy Decrease.* —

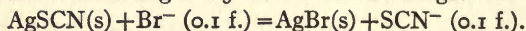
*Prob. 27.* — Calculate from the data of Prob. 39, Art. 110, the free-energy decrease attending at  $25^{\circ}$  the chemical change:



*Prob. 28.* — Calculate from the data of Prob. 41, Art. 110, the free-energy decrease, attending at  $357^{\circ}$  the change in state:



*Prob. 29.* — Calculate from the data of Prob. 54, Art. 112, the free-energy decrease attending at  $25^{\circ}$  the chemical change:



## CHAPTER XI

### THE PRODUCTION OF WORK FROM ISOTHERMAL CHANGES BY ELECTROCHEMICAL PROCESSES

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#### I. CHANGES IN STATE AND IN FREE ENERGY IN VOLTAIC CELLS

**143. Introduction.** — It has been shown in the preceding chapter that the free-energy decrease attending changes in state can be derived from the consideration of certain mechanical processes by which the changes in state take place reversibly; and thereby important relations between free energy and the equilibrium conditions of chemical reactions have been deduced. In this chapter it is shown that electrochemical processes afford another means of carrying out changes in state reversibly and hence of evaluating the free-energy decrease attending them. The changes in state occurring in voltaic cells are first considered (in Art. 144). The electromotive force of voltaic cells, the production of work by them, and the corresponding free-energy decrease are then treated (in Art. 145) in their general aspects. In the following articles these general principles are applied to the determination of the electromotive force and of the separate electrode-potentials of special types of cells.

**144. Changes in State in Voltaic Cells.** — A change in state can be made to yield electrical energy when it can be brought about by a process of reduction occurring in one place and a process of oxidation occurring in another place; for it is an inherent characteristic of reduction processes that they are attended by a liberation of positive electricity or by an absorption of negative electricity, and of oxidation processes that they are attended by the opposite electrical effects. Thus the reduction of copper-ion to metallic copper may be represented by the equation  $\text{Cu}^{++} = \text{Cu} + 2\oplus$ ; and the oxidation of metallic zinc to zinc-ion, by the equation  $\text{Zn} + 2\oplus = \text{Zn}^{++}$ , where the symbol  $\oplus$  denotes, as in Art. 63, one positive electron or one faraday of positive electricity. If these two processes occur at the same place, as is the case when metallic zinc is placed in a copper-ion solution, no electrical effect is observed. If, however, the zinc is placed in a zinc-ion solution and the copper in a copper-ion solution, and if the two solutions are placed in contact, the reduction-process tends to occur at one place and to liberate positive electricity there, and the oxidation-

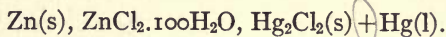
process tends to occur at another place and to absorb positive electricity there, thereby producing a difference of potential or an electromotive force between the two places; and if they are now connected by a metallic conductor, a current of electricity will flow through it, and this current can be made to produce work, for example, by passing it through an electric motor. Such an arrangement as that here described, in which an electromotive force is produced as a result of an oxidation-process and a reduction-process occurring at two different places, is known as a *voltaic cell*.

It has been shown in Art. 136 that the quantity of work that can be produced by any isothermal process is determined solely by the change in state of the system. Hence the maximum work producible by the action of a voltaic cell is fully determined by the initial and final states of the substances of which it consists; and in any case under consideration these states, or the corresponding change in state, must be exactly specified. Thus, there must be stated, in addition to the temperature, not merely the chemical reaction that takes place in the cell, but also the conditions of pressure and concentration under which the substances involved in it are produced and destroyed, and any transfers of substances from solutions of one composition to those of another composition.

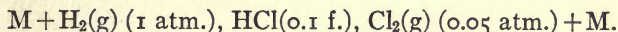
In order that there may not be a finite change in the concentrations of the solutions, and therefore in the electromotive force of the cell, during the occurrence of the change in state, it will always be considered that the solutions are present in infinite quantity, so that when a finite quantity of any substance is introduced into or withdrawn from one of the solutions of the cell there is only an infinitesimal change in its concentration. This method of consideration is much simpler for the treatment of the heat-content, free energy, and electromotive force of solutes than the closely related one, commonly employed in the formulations of the differential calculus, where the introduction of an infinitesimal quantity of the solute into a finite quantity of the solution would be considered; for it enables equivalent or molal quantities of the solute to be directly dealt with.

The character of the cell under consideration will be shown by writing the symbols of the pure substances and solutions in the order in which they are actually in contact with one another, commas being inserted to indicate the junctions at which, as will be explained later, an electromotive force is produced. The conventions described in

Arts. 109 and 129 will be employed to indicate the state of aggregation of substances and the composition of solutions. Thus a cell consisting in series of metallic zinc, of a zinc chloride solution of the composition  $\text{ZnCl}_2.100\text{H}_2\text{O}$ , and of metallic mercury covered with solid mercurous chloride, at a pressure of one atmosphere (as is always understood unless some other pressure is specified), will be represented by the expression:

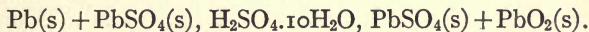


Similarly, a cell whose electrodes are an inert metal M in contact with hydrogen gas at 1 atm. and the same metal in contact with chlorine gas at 0.05 atm., and whose electrolyte is a 0.1 formal HCl solution, will be represented by the expression:

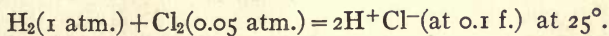
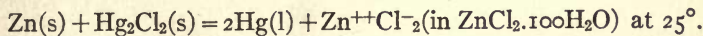


Or simply:  $\text{H}_2(1 \text{ atm.}), \text{HCl}(0.1 \text{ f.}), \text{Cl}_2(0.05 \text{ atm.}).$

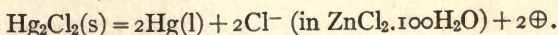
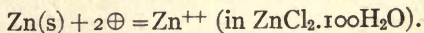
So also a lead storage-cell whose electrodes are lead and an inert metal coated with lead dioxide, and whose electrolyte is a sulfuric acid solution, say of the composition  $\text{H}_2\text{SO}_4.10\text{H}_2\text{O}$ , saturated with lead sulfate, will be represented by the expression:



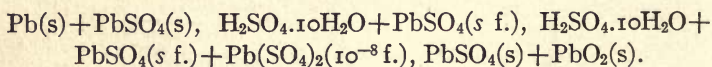
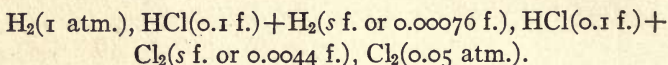
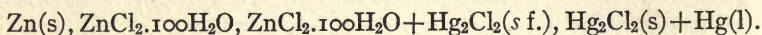
X The change in state taking place in a cell may be expressed by an equation whose left-hand member represents the initial state, and whose right-hand member represents the final state, of the substances involved in the change. Thus the changes of state occurring when at  $25^\circ$  two faradays pass from left to right (as is always understood unless the opposite is specified) through the first two cells just formulated are shown by the equations:



X The changes in state resulting from the separate electrode processes may be expressed by electrochemical equations similar to those described in Art. 63, but showing also the composition of the solutions in which the ions are produced or destroyed. Thus in the case of the first two of the above cells the changes in state at the anode and cathode may be represented by the equations:



When, as in these cells, a gaseous or a solid non-metallic substance is in contact with a metal electrode, the adjoining solution is understood to be saturated with that substance. In such cells there are therefore in reality two different solutions, even though for the sake of brevity only one may be written in formulating the cell. Thus these cells ought strictly to be represented by the following expressions, in which *s f.* denotes the formal solubility of the substance in the solution in contact with it, thus of  $\text{Hg}_2\text{Cl}_2$  in a solution of  $\text{ZnCl}_2 \cdot 100\text{H}_2\text{O}$ :



The recognition of the fact that there are in such cells two solutions of slightly different composition is of great importance in considering the mechanism of voltaic action and in evaluating the electrode-potentials discussed in Arts. 150-152.

When, as in the three cells just considered, the cell contains two solutions of substantially the same composition (in the respects that in both solutions the ions present at considerable concentrations are the same, that the concentrations of these ions are substantially the same, and that the solvent-medium as a whole is substantially the same), the ion-transferences need not be considered; for, though there is transference from the solution around one electrode to that around the other electrode, there is not an appreciable free-energy change, since the two solutions have substantially the same composition.

*Changes of State in Cells with a Single Solution. —*

*Prob. 1.* — Formulate an electrochemical equation which expresses fully the change in state that takes place at each electrode when two faradays pass through the hydrogen-chlorine cell above mentioned; and derive from these equations the expression for the change in state taking place in the cell as a whole.

*Prob. 2.* — Formulate electrochemical equations expressing the changes in state at the electrodes when two faradays pass at  $20^\circ$  through the lead storage-cell formulated above; and derive from them a corresponding expression for the change of state in the cell as a whole.

When the cell contains around the two electrodes solutions of substantially different composition, as in the cells formulated in Prob. 3, it is necessary to consider not only the processes that take

place at the two electrodes, but also the transference that occurs in the solutions; for in such cells the ion-constituents are transferred from a solution of one composition to a solution of another composition.

*Changes in State in Cells with Two Solutions. —*

*Prob. 3. —* Write equations expressing (1) the changes in state which take place as a result of the electrolysis, (2) the changes in state brought about by the transference of the ions, and (3) the resultant change in state in the cell as a whole, when one faraday passes at 18° through each of the following cells, taking 0.166 as the transference-number of the chloride-ion in the two HCl solutions:

a.  $\text{H}_2(1 \text{ atm.}), \text{HCl}(0.01 \text{ f.}), \text{HCl}(0.1 \text{ f.}), \text{H}_2(1 \text{ atm.}).$

b.  $\text{Cl}_2(1 \text{ atm.}), \text{HCl}(0.01 \text{ f.}), \text{HCl}(0.1 \text{ f.}), \text{Cl}_2(1 \text{ atm.}).$

Note that the transference effects in these cells are similar to those described in Art. 64, the left-hand solution being regarded as the anode-portion and the right-hand solution as the cathode-portion.

**145. The Production of Work and the Corresponding Decrease of Free Energy in Voltaic Cells. —** In general, when a quantity of positive electricity  $Q$  flows between two places, such as the electrodes of a voltaic cell, between which there is a fall of potential or electromotive force  $E$  in the direction of the flow, a quantity of work equal to the product  $EQ$  can be produced. Now, according to Faraday's law (Art. 62), the quantity of electricity flowing through a voltaic cell is strictly proportional to the number of equivalents  $N$  that are involved in the chemical change at each electrode; that is,  $Q = NF$ , where  $F$  represents the quantity of electricity (96,500 coulombs) that passes when a reaction involving one equivalent of each of the reacting substances takes place at each electrode. The maximum electrical work that can be obtained when  $N$  faradays of electricity pass through a voltaic cell which produces an electromotive force  $E$  is therefore equal to  $ENF$ .

When a voltaic cell acts reversibly there is ordinarily produced, in addition to the electrical work, a quantity of mechanical work corresponding to the changes in volume of the different parts of the cell taking place under their respective pressures. The total work  $W_R$  is therefore  $ENF + \Sigma(p\Delta v)$ . Since by definition (Art. 136) the free-energy decrease is equal to  $W_R - \Delta(\Sigma pv)$ , it is equal simply to the electrical work that can be produced. That is, for any change in state taking place in a voltaic cell under constant pressures:

$$-\Delta F = ENF.$$

The numerical value of the electromotive force  $E$  of the cell will in this book be given a positive sign when the cell tends to produce

a current of positive electricity through the cell in the direction in which it is written, and a negative sign when the cell tends to produce such a current in the opposite direction. The symbol  $N$  will denote the number of faradays of positive electricity that are considered to pass through the cell from left to right, its numerical value being given a negative sign when positive electricity is considered to pass in the opposite direction. The maximum electrical work and the free-energy decrease calculated by the equation will then have, as usual, a positive sign when the cell produces electrical work, and a negative sign when external work is expended upon the cell. Its value will be in joules when the electromotive force is in volts and the quantity of electricity in coulombs.

*The Maximum Work and Free-Energy Decrease Attending Changes in Voltaic Cells. —*

*Prob. 4.* — The electromotive force at  $15^\circ$  of the Daniell cell,  $\text{Zn(s)} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O(s)} \rightarrow \text{ZnSO}_4\text{(sf.)} + \text{CuSO}_4\text{(sf.)} + \text{Cu(s)}$ , is 1.093 volts. Give the value of  $NF$  in coulombs and of the electrical work in joules required to deposit 1Zn on the electrode; and state what the sign of each of these quantities signifies.

*Prob. 5.* — *a.* Calculate exact values of the electrical work and the mechanical work that are produced when 1 faraday passes under reversible conditions through the cell  $\text{H}_2(1 \text{ atm.}) \rightarrow 2\text{H}^+(0.1 \text{ f.}) + 2\text{Cl}^-(0.05 \text{ atm.})$  at  $25^\circ$ . The electromotive force of this cell is 1.451 volts. The increase in the volume of an infinite quantity of 0.1 f. HCl solution caused by introducing 1HCl into it is 18.7 ccm. *b.* Find the corresponding free-energy decrease.

## II. THE ELECTROMOTIVE FORCE OF CELLS UNDERGOING ONLY CHANGES IN CONCENTRATION OR PRESSURE

**146. Change of the Electromotive Force of Voltaic Cells with the Concentration of the Solutions.** — The considerations of the preceding articles make it possible to calculate the change that is produced in the electromotive force of a cell by varying the concentration of the solutions contained in it. Thus the difference between the electromotive forces of the cells  $\text{H}_2(1 \text{ atm.}), \text{HCl}(0.001 \text{ f.}), \text{AgCl(s)} + \text{Ag(s)}$  and  $\text{H}_2(1 \text{ atm.}), \text{HCl}(0.1 \text{ f.}), \text{AgCl(s)} + \text{Ag(s)}$  can be derived by considering that one faraday passes through these two cells arranged in series in opposition to each other, by noting what the resultant change in state is, and by equating the two expressions for the attendant free-energy decrease derived in Arts. 145 and 138.

The exact treatment of such cells is complicated by the uncertainty as to the degree of ionization of largely ionized substances and by the fact that their ions are not perfect solutes. A rough approximation to the truth is, however, secured in electrochemical calculations, as in those relating to mass-action, by employing the hypotheses that these substances are completely ionized up to moderate concentrations, such as 1 formal, and that their ions are perfect solutes. These hypotheses are to be applied to these substances in all the problems of this chapter, unless otherwise stated. The errors to which these hypotheses lead will be indicated in some cases by a comparison of the calculated with the observed values.

### *Effect of Concentration on Electromotive Force. —*

**Prob. 6.** — Calculate the difference between the electromotive forces at  $25^\circ$  of the two cells formulated in the preceding text. Compare the result with the difference between the observed electromotive forces of these cells, which are 0.5789 and 0.3522 volt.

**Prob. 7.** — Calculate the difference between the electromotive force at  $25^\circ$  of the cell  $\text{H}_2(1 \text{ atm.}), \text{HCl}(10 \text{ f.}), \text{Cl}_2(1 \text{ atm.})$  and that of the cell  $\text{H}_2(1 \text{ atm.}), \text{HCl}(6 \text{ f.}), \text{Cl}_2(1 \text{ atm.})$ . The vapor-pressures of HCl in the two solutions at  $25^\circ$  are 4.2 and 0.14 mm.

**Prob. 8.** — State what data are needed in order to calculate the electromotive force  $E_1$  at  $18^\circ$  of the cell  $\text{H}_2(1 \text{ atm.}), \text{H}_2\text{SO}_4(10 \text{ f.}), \text{O}_2(1 \text{ atm.})$  from that  $E_2$  of the cell  $\text{H}_2(1 \text{ atm.}), \text{H}_2\text{SO}_4(0.01 \text{ f.}), \text{O}_2(1 \text{ atm.})$ ; and formulate an expression by which the calculation could be made.

**Prob. 9.** — The cell  $\text{Ag(s)} + \text{AgCl(s)}, \text{HCl}(0.1 \text{ f.}), \text{Cl}_2(1 \text{ atm.})$  has at  $25^\circ$  an electromotive force of 1.135 volts. How much would its electromotive force be changed by substituting  $\text{HCl}(0.01 \text{ f.})$  for the  $\text{HCl}(0.1 \text{ f.})$ ? U. P. H<sub>2</sub>SO<sub>4</sub>

\*Measurements with such combined or double cells form the basis of one of the important methods by which values of the activity-coefficients, such as are given in the table of Art. 113, can be derived. The value of the electromotive force gives directly the free-energy decrease, and from this by equation (4) of Art. 138 the ratio of the products of the activities of the ions in the two solutions and of their activity-coefficients can be computed, as is illustrated by the following problems.

*\*Derivation of Ion-Activity-Coefficients from Electromotive Forces. —*

*\*Prob. 10. — a.* From the observed values, 0.5789 and 0.3522, for the electromotive forces of the cells formulated in the text and considered in Prob. 6, calculate the ratio of the products of the activities of hydrogen-ion and chloride-ion in 0.1 formal and in 0.001 formal HCl solution. *b.* Find the ratio of the ion-activity-coefficients at 0.1 formal and 0.001 formal, assuming that hydrogen-ion and chloride-ion have equal activities in the same solution.

*\*Prob. 11. —* At  $25^{\circ}$  0.224 volt is the electromotive force of the cell:  $\text{Hg(l)} + \text{HgO(s)}, \text{KOH(0.45 f.)}, \text{K}_n\text{Hg(l)}, \text{KOH(0.0045 f.)}, \text{HgO(s)} + \text{Hg(l)}$ , where  $\text{K}_n\text{Hg}$  represents a solution of potassium in mercury of definite but unknown concentration. Find the ratio of the ion-activity-coefficients of KOH in the two solutions, assuming that the two ions have equal activities at the same concentration.

**147. The Electromotive Force of Concentration-Cells. —** A cell which consists of two identical electrodes and of two solutions containing the same substance at two different concentrations is called a *concentration-cell*. The cell,  $\text{Zn(s)}, \text{ZnCl}_2(0.1 \text{ f.}), \text{ZnCl}_2(0.005 \text{ f.}), \text{Zn(s)}$ , is an example of a concentration-cell, as are also the cells formulated in Prob. 3, Art. 144.

The electromotive force of a concentration-cell containing the solute at small concentrations can be calculated by considering the changes in concentration that occur at each electrode as a result both of the electrolysis and the transference, when  $N$  faradays pass through it, by formulating in accordance with Art. 138 an expression for the free-energy decrease attending these concentration changes, and by equating this expression with  $ENF$ .

*Evaluation of the Electromotive Force of Concentration Cells. —*

*Prob. 12. —* Calculate the electromotive force at  $18^{\circ}$ , *a*, of the cell formulated in Prob. 3*a* above; *b*, of the cell formulated in Prob. 3*b*. *c.* Formulate general algebraic expressions involving the concentrations  $c'$  and  $c''$  and the transference-number  $\tau_A$  or  $\tau_C$ , for the electromotive force of cells like these, in which the cation, or the anion, is involved in the electrode process. *Ans. a*, 0.0192.

*Prob. 13.* — Calculate the electromotive force at  $18^{\circ}$  of the following cell, using as the transference-number that derived from the ion-conductances given in Art. 76:  $\text{Zn(s)}, \text{ZnCl}_2(0.1 \text{ f.}), \text{ZnCl}_2(0.005 \text{ f.}), \text{Zn(s)}$ .  
*Ans.* — 0.0660.

*\*Prob. 14.* — Calculate the electromotive force at  $25^{\circ}$  of the cell  $\text{Ag} + \text{AgCl}, \text{KCl}(0.5 \text{ f.}), \text{KCl}(0.05 \text{ f.}), \text{AgCl} + \text{Ag}$ , taking 0.504 as the transference-number of the chloride-ion, *a*, assuming that the salt is completely ionized and that its ions are perfect solutes; *b*, assuming that the salt has ionization values equal to the conductance-viscosity ratios as given in the table in Art. 113 and that its ions are perfect solutes; *c*, using the values of the ion-activity-coefficients given in the table in Art. 113. *d*. Tabulate these three results together with the experimentally determined value (0.0536 volt) of the electromotive force.

Another type of concentration-cell is that in which there is a single aqueous solution in contact with electrodes consisting of some metal dissolved at two different concentrations in mercury. For example, the cell  $\text{Zn.100Hg}, \text{ZnCl}_2.100\text{H}_2\text{O}, \text{Zn.200Hg}$  is of this type. Since most of the metals dissolved in mercury at small concentrations have been shown by vapor-pressure and freezing-point measurements to be nearly perfect solutes having monatomic molecules, the electromotive force of cells having such solutions as electrodes can be calculated with the aid of the preceding considerations.

A similar type of concentration-cell is that in which the two electrodes consist of some inert metal surrounded by the same gas at two different pressures, as in the oxygen cell  $\text{M} + \text{O}_2(1 \text{ atm.}), \text{KOH}(1 \text{ f.}), \text{O}_2(0.1 \text{ atm.}) + \text{M}$ .

*Electromotive Force of Cells with the Electrode Substance at Different Concentrations.* —

*Prob. 15.* — Calculate the electromotive force at  $18^{\circ}$  of the zinc-mercury cell formulated in the preceding text.

*Prob. 16.* — Calculate the electromotive force at  $25^{\circ}$  of the oxygen cell formulated in the preceding text.

### III. THE ELECTROMOTIVE FORCE OF CELLS UNDERGOING CHEMICAL CHANGES AND ITS RELATION TO THEIR EQUILIBRIUM CONDITIONS

**148. Chemical Changes in Voltaic Cells.** — In the cells thus far considered the change of state consists only in a transfer of one or more of the substances from one pressure or concentration to another. In most voltaic cells, however, a chemical change takes place. Thus in the Daniell cell the reaction  $\text{Zn(s)} + \text{CuSO}_4 = \text{Cu(s)} + \text{ZnSO}_4$  occurs. Other examples of cells in which similar chemical changes take place are given in Art. 144.

A chemical change somewhat different in character from those just considered takes place in cells whose half-cells consist, not of solid or gaseous elementary substances in contact with solutions of their ions, but of an inert metal electrode in contact with two solutes in different stages of oxidation. Thus the electrode-reactions in the cell M,  $\text{Fe}^{++}\text{Cl}^-_2(c_1) + \text{Fe}^{+++}\text{Cl}^-_3(c_2)$ ,  $\text{Cl}^-(c_3) + \text{Cl}_2(c_4)$ , M, attending the passage of one faraday are  $\text{Fe}^{++} + \oplus = \text{Fe}^{+++}$  and  $\frac{1}{2}\text{Cl}_2 = \text{Cl}^- + \oplus$ , and the whole reaction is  $\text{Fe}^{++}\text{Cl}^-_2 + \frac{1}{2}\text{Cl}_2 = \text{Fe}^{+++}\text{Cl}^-_3$ . Such cells do not, however, require special treatment; for the principles applicable to other cells can be readily extended to them, as will be seen in the following articles.

**149. The Electromotive Force of Cells in Relation to the Equilibrium Conditions of the Chemical Reactions.** — The free-energy decrease attending chemical changes between substances at any pressures or concentrations is given (as shown in Art. 145) by the general expression  $-\Delta F = \mathcal{E}NF$ , in which  $\mathcal{E}$  represents the electromotive force of a voltaic cell in which the chemical change takes place reversibly. Another form of expression for the free-energy decrease attending chemical changes between substances at small pressures or concentrations was derived in Arts. 140–142 from a consideration of their equilibrium conditions. Combination of these two expressions leads to the following relation between the electromotive force  $\mathcal{E}$  of the cell, the equilibrium-constant  $K$  of the chemical change taking place in it, and the actual concentrations,  $c_E', c_F', \dots, c_A', c_B'$ , in the cell of the chemical substances involved in the chemical change:

$$-\Delta F = \mathcal{E}NF = RT \left( \log K - \log \frac{c_E'^e c_F'^f \dots}{c_A'^a c_B'^b \dots} \right).$$

When a gaseous substance is involved in the chemical change, its actual pressure may be substituted for its concentration in the last

term of this expression; but in that case its equilibrium pressure must be correspondingly substituted in the expression for the equilibrium-constant.

This expression makes possible the calculation of equilibrium-constants from electromotive forces, or conversely that of electromotive forces from equilibrium-constants, as shown in the following problems.

*Calculation of Equilibrium-Constants from Electromotive Forces. —*

*Prob. 17.* — Calculate the dissociation-pressure in atmospheres of solid  $\text{AgCl}$  at  $25^\circ$  from the electromotive force, 1.135 volts, of the voltaic cell  $\text{Ag(s)} + \text{AgCl(s)}, \text{HCl(0.1 f.)}, \text{Cl}_2(1 \text{ atm.})$ . *Ans.*  $4.2 \times 10^{-39}$ .

*Prob. 18.* — *a.* Calculate the equilibrium-constant at  $25^\circ$  of the reaction  $\text{H}_2(\text{g}) + 2\text{AgCl(s)} = 2\text{H}^+ + 2\text{Cl}^- + 2\text{Ag(s)}$  from the electromotive force, 0.3522 volt, of the cell  $\text{H}_2(1 \text{ atm.}), \text{HCl(0.1 f.)}, \text{AgCl(s)} + \text{Ag(s)}$ . *b.* Calculate the equilibrium pressure in atmospheres of the hydrogen gas that would be produced by the action of metallic silver on 1 f.  $\text{HCl}$  solution. *Ans. b.*  $1.2 \times 10^{-12}$ .

*Prob. 19.* — *a.* From the data given in Probs. 17 and 18*a* find the electromotive force of the cell  $\text{H}_2(1 \text{ atm.}), \text{H}^+\text{Cl}^-(0.1 \text{ f.}), \text{Cl}_2(1 \text{ atm.})$ . *b.* Calculate from this electromotive force the equilibrium-constant of the reaction  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) = 2\text{H}^+ + 2\text{Cl}^-$ . *c.* Calculate this equilibrium-constant from the equilibrium-constants found in Probs. 17 and 18*a*. *Ans. b.*  $1.9 \times 10^{50}$ .

*Calculations of Electromotive Forces from Equilibrium-Constants. —*

*Prob. 20.* — *a.* Calculate the electromotive force at  $25^\circ$  of the cell  $\text{H}_2(1 \text{ atm.}), \text{H}_2\text{SO}_4(0.01 \text{ f.}), \text{O}_2(1 \text{ atm.})$  from the equilibrium-constant at  $25^\circ$  of the reaction  $2\text{H}_2\text{O(g)} = 2\text{H}_2(\text{g}) + \text{O}_2(\text{g})$ , which has been indirectly derived from equilibrium measurements at higher temperature and found to have the value  $9.7 \times 10^{-81}$ . The vapor-pressure of water at  $25^\circ$  is 24 mm. *b.* Calculate the minimum electrical energy required to decompose  $1\text{H}_2\text{O}$  by the electrolysis of a 0.1 f.  $\text{KOH}$  solution at  $25^\circ$  under a barometric pressure of 784 mm. *Ans. a,* 1.228.

*Prob. 21.* — *a.* Calculate the electromotive force at  $25^\circ$  of the cell  $\text{Cl}_2(1 \text{ atm.}), \text{HCl(10 f.)}, \text{O}_2(1 \text{ atm.})$  from the equilibrium-constant of the reaction  $4\text{HCl(g)} + \text{O}_2(\text{g}) = 2\text{H}_2\text{O(g)} + 2\text{Cl}_2(\text{g})$ , which has been derived from measurements at higher temperatures of the equilibrium of this reaction (involved in the Deacon process of producing chlorine), and found to have at  $25^\circ$  the value  $1.0 \times 10^{13}$ . The vapor-pressures at  $25^\circ$  of  $\text{H}_2\text{O}$  and  $\text{HCl}$  in 10 f.  $\text{HCl}$  solution are 9.4 mm. and 4.2 mm., respectively. *b.* Assuming the process could be made reversible, calculate how much electrical energy might be obtained in producing 1 mol of chlorine gas by an electric current passing through a 10 f.  $\text{HCl}$  solution at  $25^\circ$  between electrodes of an inert metal under a barometric pressure of 750 mm., the solution around the cathode being kept saturated with air. *Ans. a,* 0.1151.

## IV. ELECTRODE-POTENTIALS AND LIQUID-POTENTIALS

**150. The Nature of Electrode-Potentials.** — The electromotive force produced by a voltaic cell is the sum of the electromotive forces produced at the junctions between the electrodes and the solutions and of the electromotive forces produced at the junctions between the different solutions that may be present in the cell. Thus the electromotive force of the Daniell cell is the algebraic sum of the electromotive force from the zinc to the zinc sulfate solution, that from the zinc sulfate solution to the copper sulfate solution, and that from the copper sulfate solution to the copper. The electromotive forces at the electrodes are commonly called *electrode-potentials*; and those at the junctions of the solutions, *liquid-potentials* (or *diffusion-potentials*).

The consideration of these partial electromotive forces is important in the respects that it shows more clearly the separate factors which determine electromotive force and the mechanism by which it is produced; that it enables the electromotive force of a large number of cells to be calculated from a small number of experimentally determined constants; and that it affords a simple means of predicting the equilibrium conditions of oxidation and reduction reactions. The factors on which electrode-potentials depend will be first considered.

Like ordinary chemical changes, the electrochemical reactions that occur at electrodes have definite equilibrium conditions, and take place in one direction or the other till these conditions are satisfied. For example, when a neutral plate of copper is placed in a 0.1 formal  $\text{CuSO}_4$  solution at  $25^\circ$ , the equilibrium conditions of the reaction  $\text{Cu(s)} + 2\oplus = \text{Cu}^{++}$  require that copper ions deposit on the plate. This gives the plate a positive charge, and raises it to a higher potential than the solution. This creates a counter electromotive force which tends to drive positive electricity, and therefore the positively charged copper ions, back into the solution. Equilibrium is established when this counter electromotive force just compensates the electromotive force arising from the mass-action tendency of the copper ions to deposit. In other cases the tendency of the reaction to take place may produce an electromotive force directed from the metal to the solution. For example, in order to satisfy the equilibrium conditions of the reaction  $\text{Zn(s)} + 2\oplus = \text{Zn}^{++}$ , zinc placed in contact with 0.1 formal  $\text{ZnSO}_4$  solution must pass into the solution as zinc ions until enough positive electricity accumulates in the layer of solution adjoining the electrode to produce a counter electromotive force equal to that

corresponding to the tendency of the zinc to pass into solution. In general, starting with a definite concentration of the ion and definite pressure of the gas (in case a gas is involved) at a definite temperature and with electrically neutral conditions, the reaction will proceed on the surface of the electrode in one direction or the other till enough positive or negative electricity is accumulated on the electrode and withdrawn from the adjoining layer of solution to produce a potential-difference sufficiently great to compensate the inherent tendency of the chemical reaction to take place.

The quantity of ion that has to deposit on the electrode or be produced in the solution in order to bring the electrode to the equilibrium potential, which seldom exceeds one or two volts, is however extremely small, owing to the very large value of the faraday in relation to the quantity of electricity which produces considerable electrostatic effects. Thus when a large glass flask containing dilute sulfuric acid is coated on the outside with tinfoil and the latter is charged with positive electricity at 1000 volts, and when a capillary mercury electrode is inserted in the acid solution and this electrode is connected to earth, it is found that a bubble of gas consisting of  $10^{-10}$  equivalent of hydrogen is set free on the surface of the mercury.

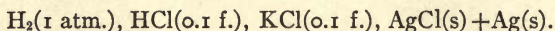
**151. The Expression of Electrode-Potentials.** — Although attempts have been made to determine by various experimental methods the absolute values of electrode-potentials, yet the measurements made by these methods are not nearly so accurate nor reliable as those of the electromotive force of ordinary cells. It is therefore customary to adopt as the value of the electrode-potential of any half-cell (such as  $\text{Zn(s)}, \text{ZnCl}_2.100\text{H}_2\text{O}$ ) the electromotive force of a whole cell which consists of the half-cell under consideration combined with a standard half-cell. The electrode-potential of the standard half-cell is thereby arbitrarily assumed to be zero. Various half-cells have been used as such standards of reference; but it has now become a fairly uniform practice to employ the *molal hydrogen electrode*, which consists of hydrogen gas at a partial pressure of one atmosphere in contact, with the aid of an inert metal electrode (such as platinized platinum), with an aqueous solution 1 molal in hydrogen-ion. This half-cell is represented by the formula  $\text{H}_2(1 \text{ atm.}), \text{H}^+(1 \text{ m.})$ . In this book this half-cell will always be used as the standard of reference; it being further specified that the solution has such a hydrogen-ion concentration that it produces the same thermodynamic and mass-action

effects as a solution containing 1 mol of hydrogen-ion per 1000 grams of water would produce if the hydrogen-ion were a perfect solute at that concentration. (\* In other words, the activity as defined in Art. 113, not the concentration, of the hydrogen-ion is to be 1 molal.) The *electrode-potential* of any half-cell is therefore equal to the electromotive force of the whole cell formed by combining it with this standard half-cell. Thus the electrode-potential of the half-cell  $\text{Zn(s)}, \text{ZnCl}_2.100\text{H}_2\text{O}$  is equal to the electromotive force of the whole cell  $\text{Zn(s)}, \text{ZnCl}_2.100\text{H}_2\text{O} \parallel \text{H}^+(1 \text{ m.}), \text{H}_2(1 \text{ atm.})$ ; and the electrode-potential of the half-cell  $\text{Cl}_2(1 \text{ atm.}), \text{HCl}(0.1 \text{ f.})$  is equal to the electromotive force of the cell  $\text{Cl}_2(1 \text{ atm.}), \text{HCl}(0.1 \text{ f.}) \parallel \text{H}^+(1 \text{ m.}), \text{H}_2(1 \text{ atm.})$ . It is, however, further understood that in evaluating this electromotive force the liquid-potential between the two solutions has been subtracted from the measured electromotive force of the whole cell — a fact which is indicated in the formulation of the cell by inserting parallel lines, instead of a comma, at the liquid junction, as is done in the cells just considered.

It follows from these conventions that the electrode-potential has a positive sign when positive electricity tends to flow from the electrode to the solution, and a negative sign when it tends to flow in the reverse direction. In using data from outside sources, it is to be noted that foreign electrochemists employ the opposite convention as to the sign of electrode-potentials.

In the case of liquid-potentials the convention here adopted is the same as in the case of whole cells; namely, the liquid-potential is given a positive sign when positive electricity tends to flow from the solution whose symbol is written on the left-hand side to the solution whose symbol is written on the right-hand side; and it is given a negative sign in the reverse case.

*Prob. 22. — Conventions Relating to Electrode-Potentials and Liquid-Potentials. — a.* Formulate the whole cell whose electromotive force is equal to the electrode-potential of the half-cell  $\text{Ag(s)} + \text{AgCl(s)}, \text{KCl}(0.1 \text{ f.})$ . *b.* From the facts that at  $25^\circ$  this electrode-potential is  $-0.289$  volt and that of  $\text{H}_2(1 \text{ atm.}), \text{HCl}(0.1 \text{ f.})$  is  $0.064$  volt, and that the liquid-potential of  $\text{KCl}(0.1 \text{ f.}), \text{HCl}(0.1 \text{ f.})$  is  $-0.028$  volt, calculate the electromotive force of the cell

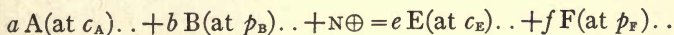


**152. Change of Electrode-Potentials with the Ion-Concentrations, and the Concept of Molal Electrode-Potentials.** — Just as the total

electromotive force of a cell is determined solely by the change in state that takes place in it, so any electrode-potential is determined solely by the change in state that takes place at the electrode. With the aid of this principle, by equating the two general expressions for free-energy decrease derived in Arts. 138 and 145, the change of an electrode-potential with the concentration of the ions or with that of any other gaseous or dissolved substance involved in the electrode reaction can be formulated, as shown by the following problems, provided the concentrations are so small that the dissolved substances behave as perfect solutes.

*Prob. 23. — Change of Electrode-Potential with the Concentration or Pressure of the Substances Involved in the Electrode Reaction. — a.* Formulate an electrochemical equation expressing fully the change in state that occurs when two faradays pass from the electrode to the solution in the half-cell  $\text{Cl}_2(p \text{ atm.})$ ,  $\text{Cl}^-(c \text{ m.})$ , and give an expression for the free-energy decrease in terms of its electrode-potential  $E$ . *b.* Describe a process of producing this same change in state which involves three steps, of which one is brought about with the aid of half-cell  $\text{Cl}_2(1 \text{ atm.})$ ,  $\text{Cl}^-(1 \text{ m.})$ , whose electrode-potential is  $\tilde{E}$ , and formulate expressions for the free-energy decrease that attends each of the three steps of the process and the process as a whole, regarding the substances as perfect solutes. *c.* Combine these results, in accordance with the law of initial and final states, so as to give an expression for the difference in the electrode-potentials of the two half-cells.

The electrode-potential of a half-cell in which all the substances taking part in the electrode reaction are considered to be perfect solutes at a concentration of 1 molal or perfect gases at a pressure of 1 atm. is called the *molal electrode-potential*  $\tilde{E}$  of the half-cell. The electrode-potential  $E$  of any half-cell in which the electrode reaction is expressed by the equation:



is related to the molal electrode-potential  $\tilde{E}$  of the reaction in the way shown by the general expression:

$$E = \tilde{E} - \frac{RT}{nF} \log \frac{c_E^e \dots p_F^f \dots}{c_A^a \dots p_B^b \dots}$$

This equation holds true strictly only for perfect solutes and perfect gases, and approximately for solutes or gases only at moderate concentrations or pressures; and correspondingly, the molal electrode-potential is not that actually observed when the concentrations of the

solutes are 1 molal, but is the value calculated by the equation for the concentration 1 molal from the electrode-potentials of half-cells containing the solutes at much smaller concentrations. (\*In other words, the molal electrode-potential refers strictly to an activity, not to a concentration, of 1 molal.) In the problems of this chapter, however, unless otherwise stated, largely ionized substances are as an approximation to be regarded as completely ionized, and their ions are to be treated as perfect solutes up to a concentration of 1 molal.

For convenience in numerical calculations it may be noted that, when ordinary logarithms are used, the coefficient  $2.303RT/NF$  preceding the logarithmic term has the value  $1.984 \times 10^{-4}T/N$  volt, or at  $25^\circ$  the value  $0.05915/N$  volt. This last number, approximately 0.059 volt, is evidently the amount by which the electrode-potential at  $25^\circ$  changes when the molality of any univalent ion involved in the electrode reaction is varied tenfold.

*Relation between Actual and Molal Electrode-Potentials. —*

*Prob. 24.* — Derive by a consideration like that employed in Prob. 23 the general expression given above.

*Prob. 25.* — Write the electrochemical reaction that takes place when electricity passes from the electrode to the solution in each of the following half-cells, where the molalities of the solutes are represented (as in mass-action expressions) by their chemical formulas enclosed within parentheses; and formulate the corresponding expression for the relation between the molal electrode-potential and the actual electrode potential at these molalities:

- a.  $\text{Zn(s)}, \text{Zn}^{++}$  at  $(\text{Zn}^{++})$  m.
- b.  $\text{M}, \begin{cases} \text{Cl}^- \text{ at } (\text{Cl}^-) \text{ m.} \\ \text{Cl}_2 \text{ at } (\text{Cl}_2) \text{ m.} \end{cases}$
- c.  $\text{M}, \begin{cases} \text{OH}^- \text{ at } (\text{OH}^-) \text{ m.} \\ \text{O}_2 \text{ at } p_{\text{O}_2} \text{ atm.} \end{cases}$
- d.  $\text{M}, \begin{cases} \text{Fe}^{++} \text{ at } (\text{Fe}^{++}) \text{ m.} \\ \text{Fe}^{+++} \text{ at } (\text{Fe}^{+++}) \text{ m.} \end{cases}$
- e.  $\text{Hg(l)} + \text{Hg}_2\text{SO}_4(\text{s}), \text{SO}_4^{--}$  at  $(\text{SO}_4^{--})$  m.
- f.  $\text{M}, \begin{cases} \text{Hg}_2^{++} \text{ at } (\text{Hg}_2^{++}) \text{ m.} + \text{Cl}^- \text{ at } (\text{Cl}^-) \text{ m.} \\ \text{HgCl}_2 \text{ at } (\text{HgCl}_2) \text{ m.} \end{cases}$
- g.  $\text{M}, \begin{cases} \text{MnO}_4^{--} \text{ at } (\text{MnO}_4^{--}) \text{ m.} \\ \text{MnO}_4^- \text{ at } (\text{MnO}_4^-) \text{ m.} \end{cases}$

*Prob. 26.* — The potential of a platinum electrode in an acid solution of potassium iodate and iodine is found to depend only on the concen-

trations of  $\text{H}^+$ ,  $\text{IO}_3^-$ , and  $\text{I}_2$ . *a.* Write the electrode-reaction attending the passage of electricity from the electrode to the solution. *b.* Formulate an expression by which the electrode-potential at  $25^\circ$  for any small concentrations ( $\text{H}^+$ ), ( $\text{IO}_3^-$ ), ( $\text{I}_2$ ) could be calculated from the molal electrode-potential.

*Evaluation of Molal Electrode-Potentials. —*

*Prob. 27.* — Calculate an approximate value, under the assumption of complete ionization, of the molal electrode-potential of  $\text{Zn(s)}$ ,  $\text{Zn}^{++}$  from the fact that the cell  $\text{Zn(s)}, \text{ZnCl}_2(0.01 \text{ f.}), \text{HCl}(0.02 \text{ f.}), \text{H}_2(\text{g})$  has at  $25^\circ$  an electromotive force of 0.695 volt, when the hydrogen gas is slowly passed under a barometric pressure of 754 mm. through the  $\text{HCl}$  solution. The vapor-pressure of water at  $25^\circ$  is 24 mm., and the liquid-potential in the cell is estimated to be  $-0.030$  volt. *Ans.* 0.766.

*Prob. 28.* — Calculate the molal electrode-potential at  $25^\circ$ , *a.* of  $\text{Ag(s)} + \text{AgCl(s)}, \text{Cl}^-$ , and *b.* of  $\text{Ag(s)}, \text{Ag}^+$ , from the facts that the cell  $\text{H}_2(1 \text{ atm.}), \text{HCl}(0.1 \text{ f.}), \text{AgCl(s)} + \text{Ag(s)}$  has at  $25^\circ$  an electromotive force of 0.3522 volt and the solubility of silver chloride at  $25^\circ$  is  $1.30 \times 10^{-5}$  formal. Consider the acid to be completely ionized and its ions to be perfect solutes. *Ans.* *a.*  $-0.234$ ; *b.*  $-0.812$ .

*\*Prob. 29.* — Compute more exact values of the two molal electrode-potentials calculated in *Prob. 28*, taking into account the activity-coefficient of the ions in the  $\text{HCl}$  solution, as given in the table of Art. 113. *Ans.* *a.*  $-0.223$ ; *b.*  $-0.801$ .

*\*Prob. 30.* — *Electrode-Potential of the Normal Calomel Electrode.* — Calculate the electrode-potential of  $\text{Hg(l)} + \text{Hg}_2\text{Cl}_2(\text{s}), \text{KCl}(1 \text{ n.})$  at  $25^\circ$  from the following data: The molal electrode-potential of  $\text{Hg(l)} + \text{Hg}_2\text{Cl}_2(\text{s}), \text{Cl}^-$  has been computed to be  $-0.270$  volt by the method illustrated by *Prob. 28*; a 1 n.  $\text{KCl}$  solution is 1.033 f. in  $\text{KCl}$ ; and the ion-activity coefficient of  $\text{KCl}$  in this solution is 0.633. *Ans.*  $-0.281$ .

The difference,  $-0.281$  volt, between the electrode-potential of the *normal calomel electrode*, which is the half-cell represented by the formula  $\text{Hg(l)} + \text{Hg}_2\text{Cl}_2(\text{s}), \text{KCl}(1 \text{ n.})$ , and that of the molal hydrogen electrode is a quantity of much practical importance, since other electrode-potentials are often measured directly against the normal calomel electrode, instead of against a hydrogen electrode, because of greater experimental convenience and because the liquid-potentials involved are usually much smaller.

**153. Values of the Molal Electrode-Potentials.** — The following table contains some of the more accurately determined values of the molal electrode-potentials at  $25^\circ$  and one atmosphere, referred to that of the molal hydrogen electrode taken as zero.

## MOLAL ELECTRODE-POTENTIALS AT 25°.

Reduced state	Oxidized state	Electrode-potential	Reduced state	Oxidized state	Electrode-potential
Li	Li <sup>+</sup>	2.958	Cu + Cl <sup>-</sup>	CuCl(s)	-0.119
Rb	Rb <sup>+</sup>	2.924	Ag + Cl <sup>-</sup>	AgCl(s)	-0.224
K	K <sup>+</sup>	2.922	Hg + Cl <sup>-</sup>	$\frac{1}{2}$ Hg <sub>2</sub> Cl <sub>2</sub> (s)	-0.270
Na	Na <sup>+</sup>	2.713	Cu	Cu <sup>++</sup>	-0.345
Zn	Zn <sup>++</sup>	0.758	2OH <sup>-</sup>	$\frac{1}{2}$ O <sub>2</sub> + H <sub>2</sub> O	-0.399
Fe	Fe <sup>++</sup>	0.441	Cu	Cu <sup>+</sup>	-0.47
Cd	Cd <sup>++</sup>	0.398	I <sup>-</sup>	$\frac{1}{2}$ I <sub>2</sub> (s)	-0.536
Tl	Tl <sup>+</sup>	0.336	Fe <sup>++</sup>	Fe <sup>+++</sup>	-0.747
Sn	Sn <sup>++</sup>	0.136	Hg(l)	$\frac{1}{2}$ Hg <sub>2</sub> <sup>++</sup>	-0.799
Pb	Pb <sup>++</sup>	0.122	Ag	Ag <sup>+</sup>	-0.800
H <sub>2</sub> (g)	2H <sup>+</sup>	0.000	Br <sup>-</sup>	$\frac{1}{2}$ Br <sub>2</sub> (1 m.)	-1.085
			Cl <sup>-</sup>	$\frac{1}{2}$ Cl <sub>2</sub> (g)	-1.359

**154. Derivation of Related Molal Electrode-Potentials from One Another.** — Molal electrode-potentials that are related to one another can be calculated in the ways illustrated by the following problems.

*Prob. 31. — Molal Electrode-Potentials Corresponding to Different States of Aggregation.* — Calculate the molal electrode-potential at 25° a, of Cl<sub>2</sub> (1 m.), Cl<sup>-</sup>, and b, of I<sub>2</sub> (1 m.), I<sup>-</sup>, from the values given for Cl<sub>2</sub>(g), Cl<sup>-</sup>, and for I<sub>2</sub>(s), I<sup>-</sup>, in the table of Art. 153, and from the molalities, 0.062 and 0.0013, of Cl<sub>2</sub> and I<sub>2</sub> in water saturated with them at 25° when the pressure is 1 atm. *Ans. a, -1.395; b, -0.621.*

*Prob. 32. — Molal Electrode-Potential of a Metal in the Presence of One of Its Slightly Soluble Salts.* — Calculate the molal electrode-potential at 25° of Hg(l) + Hg<sub>2</sub>SO<sub>4</sub>(s), SO<sub>4</sub><sup>-</sup>, from that of Hg(l), Hg<sub>2</sub><sup>++</sup> given in the table, and from the solubility-product (Hg<sub>2</sub><sup>++</sup>) × (SO<sub>4</sub><sup>-</sup>) of Hg<sub>2</sub>SO<sub>4</sub> which at 25° is 8.2 × 10<sup>-7</sup>. *Ans. -0.62 volt.*

*Prob. 33. — Molal Electrode-Potentials of an Element that Exists in more than Two States of Oxidation.* — a. By considering the changes in state that occur on passing electricity at 25° through the voltaic cells Cu, Cu<sup>+</sup>(1 m.) || Cu<sup>++</sup>(1 m.), Cu, and Cu, Cu<sup>++</sup>(1 m.) ||  $\left\{ \begin{array}{l} \text{Cu}^+ (1 \text{ m.}) \\ \text{Cu}^{++} (1 \text{ m.}) \end{array} \right\}, \text{M}$ , derive a relation between the molal electrode-potentials of Cu(s), Cu<sup>+</sup>; Cu(s), Cu<sup>++</sup>; and Cu<sup>+</sup>, Cu<sup>++</sup>. b. Calculate the last of these potentials from the first two. *Ans. b, -0.22.*

**155. The Electromotive Force of Cells with Dilute Solutions in Relation to the Molal Electrode-Potentials.** — The electromotive force of cells in which the liquid-potentials are negligible or for theoretical purposes are to be disregarded can be calculated from the molal electrode-potentials in the way illustrated by the following problems.

*Evaluation of Electromotive Forces. —*

*Prob. 34.* — Calculate the electromotive force at  $25^\circ$  of the cell  $\text{Zn(s)}, \text{ZnCl}_2(0.001 \text{ f.}), \text{AgCl(s)} + \text{Ag(s)}$ .

*Prob. 35.* — Calculate the electromotive force at  $25^\circ$  of the cell  $\text{H}_2(0.1 \text{ atm.}), \text{HCl}(0.1 \text{ f.}), \text{PbCl}_2(\text{s}) + \text{Pb(s)}$ . The saturated solution of  $\text{PbCl}_2$  in water at  $25^\circ$  is 0.039 formal.

*Prob. 36.* — Formulate numerical expressions for calculating the electromotive force at  $25^\circ$  of each of the following cells:

*a*,  $\text{M} + \text{CuCl(s)}, \text{CuCl}_2(0.01 \text{ f.}), \text{Cl}_2(0.1 \text{ atm.})$ .

*b*,  $\text{M}, 0.01 \text{ f. KI sat. with I}_2 \parallel \left\{ \begin{array}{l} \text{FeCl}_2(0.02 \text{ f.}) \\ \text{FeCl}_3(0.01 \text{ f.}) \end{array} \right\}, \text{M}$ .

The solubility-product of  $\text{CuCl}$  is  $1.2 \times 10^{-6}$  formal. For the composition of iodide solutions saturated with iodine see *Prob. 45, Art. 111*.

**156. The Electromotive Force of Cells with Concentrated Solutions.**

—The electromotive force of any cell in which solutes are present at large concentrations cannot be calculated from the molal electrode-potentials with the aid of the logarithmic concentration formula of *Art. 152*, since this holds true even approximately only when the concentration does not exceed 1 formal. A knowledge of the change in state taking place in such a cell and of the reactions occurring at its electrodes is, however, of importance, since it shows qualitatively the factors which determine the magnitude of the electromotive force. This is illustrated by the following problems, which relate to certain cells of technical importance.

*Prob. 37.* — *The "Dry Cell."* — The Leclanché cell and the common "dry cell," which is a Leclanché cell to which some porous material, such as paper-pulp or sawdust, has been added, consists essentially of a zinc rod (amalgamated to diminish local voltaic action) dipping into a concentrated  $\text{NH}_4\text{Cl}$  solution containing  $\text{ZnCl}_2$ , and a carbon rod coated with  $\text{MnO}_2$  dipping into the same solution. *a*. Formulate the cell and the reaction that takes place at each electrode and the whole reaction in the cell, taking into account the facts that the  $\text{MnO}_2$  is reduced to  $\text{Mn}_2\text{O}_3$ , and that  $\text{Zn(OH)}_2$  is soluble in  $\text{NH}_4\text{Cl}$  solution with formation of  $\text{Zn(NH}_4)_4\text{Cl}_2$ . *b*. Show in what direction the electromotive force would be changed by decreasing the concentration of the  $\text{NH}_4\text{Cl}$ .

*Prob. 38.* — *The Edison Storage Cell.* — In the nickel-iron (Edison) storage cell,  $\text{Fe(s)} + \text{Fe(OH)}_2(\text{s}); \text{KOH}(21\%), \text{Ni(OH)}_2(\text{s}) + \text{Ni(OH)}_3(\text{s})$ , the main reaction is  $\text{Fe(s)} + 2\text{Ni(OH)}_3(\text{s}) = \text{Fe(OH)}_2(\text{s}) + 2\text{Ni(OH)}_2(\text{s})$  (the degree of hydration of the three oxides being, however, somewhat indefinite). *a*. Write the reaction occurring at each electrode. *b*. Show in what direction each of the electrode-potentials, and also the electromotive force of the whole cell, would vary with increase of the  $\text{KOH}$  concentration.

*\*Prob. 39. — The Clark Standard Cell.* — One form of the Clark cell, used as a standard cell in electromotive force measurements is at  $20^{\circ}$  represented by the formula:  $\text{Zn(s)} + \text{ZnSO}_4 \cdot 7\text{H}_2\text{O(s)}, \text{ZnSO}_4 \cdot 16.8\text{H}_2\text{O}, \text{Hg}_2\text{SO}_4\text{(s)} + \text{Hg(l)}$ . *a.* Specify the change of state that occurs when two faradays pass through the cell. *b.* Show that even in an actual cell, with only a finite quantity of solution, no variation of the electromotive force results when two faradays pass, provided the change in state takes place slowly enough. *c.* Explain how the electromotive force of the cell would be changed by making the saturated  $\text{ZnSO}_4$  solution also 1 formal in  $\text{Na}_2\text{SO}_4$ .

**157. The Nature of Liquid-Potentials and Expressions for their Approximate Evaluation.** — The electromotive force at the boundary between two solutions arises from the different rates at which the positive and negative ions tend to diffuse from one solution into the other.

This principle may be first illustrated by applying it to solutions of the same substance at two different concentrations, such as  $\text{HCl}$  (1 f.),  $\text{HCl}$ (0.1 f.). In this case both kinds of ions diffuse from the first to the second solution in consequence of their smaller concentrations in the latter solution; but, owing to their greater mobility, the hydrogen ions tend to pass into the second solution in larger quantity, and they do so to a slight extent, until such an excess of positive electricity is accumulated in the intermediate layers that the unequal diffusion-rates of the two ions are compensated by the effect of the potential-gradient in driving the positive hydrogen ions backward and drawing the negative chloride ions forward. The result of the different diffusion-rates of the two ions is in this case evidently an electromotive force directed from the more concentrated to the more dilute  $\text{HCl}$  solution.

Similar considerations apply to solutions of two different substances at the same concentration, such as  $\text{HCl}$ (1 f.),  $\text{NaCl}$ (1 f.). In this case, the hydrogen ions evidently tend to diffuse from the first solution to the second, and the sodium ions in the reverse direction; but owing to the much greater mobility of the hydrogen ions there is a resultant flow of positive electricity, and correspondingly an electromotive force, from the  $\text{HCl}$  to the  $\text{NaCl}$  solution. As before, there can be only a very slight accumulation of hydrogen ions in the boundary of the second solution because of the counter electromotive force thereby produced.

*Prob. 40. — The Nature and Direction of Liquid-Potentials. — a.* Explain fully, in accordance with the above statements, the mechanism of the process by which a liquid-potential results in the case of KOH(1 f.), KCl(1 f.). *b.* Predict the sign of the liquid-potential of NaOH(1 f.), NaOH(0.1 f.); and of NaCl(1 f.), KNO<sub>3</sub>(1 f.).

Expressions by which liquid-potentials can be approximately evaluated can be derived either by formulating quantitatively the above considerations with the aid of the laws of diffusion, or by applying the free-energy principles in the way shown in Art. 158 to the changes in state taking place at the boundary.

By these methods the following expressions for the liquid-potential  $E_L$ , in terms of the ion-conductances,  $\Lambda_c$ ,  $\Lambda_c'$ ,  $\Lambda_a$ , etc., and the number of charges or valences,  $\nu_a$  and  $\nu_c$ , of the cation and anion, have been derived under the assumptions that the substances are completely ionized and that their ions are perfect solutes and have constant mobilities equal to those at zero concentration:—

For combinations of the ionic types  $C^+A^-$  (at  $c_1$ ),  $C^+A^-$  (at  $c_2$ );  $C^+_2A^-$  (at  $c_1$ ),  $C^+_2A^-$  (at  $c_2$ ); etc:

$$E_L = \frac{\frac{\Lambda_c}{\nu_c} - \frac{\Lambda_a}{\nu_a}}{\Lambda_c + \Lambda_a} \frac{RT}{F} \log \frac{c_1}{c_2}. \quad (1)$$

For combinations of the types  $CA$ ,  $C'A$ ;  $C_2A$ ,  $C'_2A$ ;  $CA_2$ ,  $C'A_2$ ; etc., in which the two substances are at the same concentrations:

$$E_L = \frac{RT}{\nu_c F} \log \frac{\Lambda_c + \Lambda_a}{\Lambda_c' + \Lambda_a}. \quad (2)$$

For combinations of the types  $CA$ ,  $C'A$ ;  $C_2A$ ,  $C'_2A$ ;  $CA_2$ ,  $CA'_2$ ; etc., in which the two substances have the same concentrations:

$$E_L = - \frac{RT}{\nu_a F} \log \frac{\Lambda_c + \Lambda_a}{\Lambda_c + \Lambda_a'}. \quad (3)$$

#### *Evaluation of Liquid Potentials. —*

*Prob. 41. —* Calculate the liquid-potential at 18° of the combinations: *a*, NaCl(0.1 f.), NaCl(0.01 f.); *b*, K<sub>2</sub>SO<sub>4</sub>(0.1 f.), K<sub>2</sub>SO<sub>4</sub>(0.01 f.).

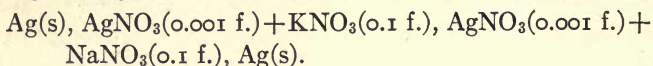
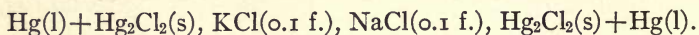
*Prob. 42. —* Calculate the liquid-potential at 25° of: *a*, KOH(0.1 f.), KCl(0.1 f.); *b*, HCl(0.01 f.), KCl(0.01 f.); *c*, ZnSO<sub>4</sub>(0.1 f.), CuSO<sub>4</sub>(0.1 f.).

*Prob. 43. —* Calculate the electromotive force at 25° of the cell Ag(s), AgNO<sub>3</sub>(c.1 f.), KNO<sub>3</sub>(0.1 f.), KCl(0.1 f.), KCl(1 f.) + Hg<sub>2</sub>Cl<sub>2</sub>(s), Hg(l).

For combinations of solutions of two salts having a common ion but different concentrations, such as KNO<sub>3</sub>(0.1 f.), KCl(1 f.), and

for combinations of solutions of salts without a common-ion, such as  $\text{KNO}_3(0.1 \text{ n.})$ ,  $\text{NaCl}(0.01 \text{ n.})$ , the calculation of the liquid-potential is more complicated. Combinations of these kinds can, however, be avoided, as illustrated by the cell of Prob. 43, by connecting the two solutions through intermediate ones so as to produce only combinations of the two types for which the liquid-potentials can be calculated by the above equations.

A liquid-potential can sometimes be experimentally determined by measuring the electromotive force of a cell involving it in which the two electrode-potentials are made substantially equal, as in the cells:



*Prob. 44.* — *a.* Show that the electromotive force of the silver cell just formulated is substantially equal to the liquid-potential of  $\text{KNO}_3(0.1 \text{ f.})$ ,  $\text{NaNO}_3(0.1 \text{ f.})$ , by specifying exactly what determines each of the three partial potentials of the cell. *b.* State what assumption is involved in regarding the two electrode-potentials equal to each other.

**\*158. Derivation of the Liquid-Potential Equations.** — Just as the electromotive force of a whole cell is determined by the free-energy decrease attending the change in state that takes place in the cell, and just as the electrode-potential is determined by the free-energy decrease attending the change in state that takes place at the electrode, so a liquid-potential is determined by the free-energy decrease attending the change in state that takes place at the boundary between the two solutions.

The change in state at such a boundary is of a simple character in the case where the two solutions contain only the same solute at two different concentrations, as in the combination,  $\text{HCl}(0.01 \text{ f.})$ ,  $\text{HCl}(0.1 \text{ f.})$ . In this case, in order to derive equation (1) of Art. 157 for the liquid-potential, it is only necessary to consider the number of equivalents of the positive ion-constituent and of the negative ion-constituent that pass through the boundary in the two opposite directions per faraday passed through, to formulate the free-energy decrease attending these transfers, on the one hand, in terms of the electrical work  $E_{\text{LF}}$  involved when they are brought about by the passage of one faraday, and on the other hand, in terms of the usual logarithmic concentration equations of Art. 138, and to equate these two expressions. This derivation involves the assumptions that the

solute is completely ionized, that its ions behave as perfect solutes, and that the ratio of their mobilities, that is, the transference-number, is constant up to the highest concentration involved.

*Derivation of the Equation for the Liquid-Potential between Solutions with the Same Solute at Different Concentrations. —*

*Prob. 45.* — Derive equation (1) of Art. 157 in the form it assumes for a univalent solute at two different concentrations, such as HCl(at  $c_1$ ), HCl(at  $c_2$ ), making the assumptions stated in the text.

*Prob. 46.* — Derive equation (1) of Art. 157 in the form it assumes for a univalent solute at two different concentrations, such as CaCl<sub>2</sub>(at  $c_1$ ), CaCl<sub>2</sub>(at  $c_2$ ), making the assumptions stated in the text.

It will be evident from these derivations that, provided only that the ratio of the two ion-conductances, and hence the transference-number  $T_C$  or  $T_A$ , does not vary between the two concentrations involved, and that the two ions can be considered to have the same activity-coefficient  $\alpha$  in the same solution, an exact expression for the liquid-potential is given in the case of a univalent solute by the equation:

$$E_{LF} = (T_C - T_A) RT \log \frac{c_1 \alpha_1}{c_2 \alpha_2}.$$

By a similar consideration of the ion-transference that takes place at the boundary of the two solutions and with the aid of the same assumptions, an expression can be derived for the liquid-potential of combinations of the types KCl, HCl; K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>; ZnSO<sub>4</sub>, CuSO<sub>4</sub>. Namely, taking as a specific example the combination KCl(at  $c$ ), HCl(at  $c$ ), it will be noted that there must be at the boundary an intermediate portion of the solution in which the two substances are present in varying proportions, the concentration of the potassium chloride decreasing continuously from left to right from  $c$  to 0, and that of the hydrogen chloride increasing continuously in the same direction from 0 to  $c$ . Considering now within the boundary-portion any two adjoining layers of infinitesimal length in which at equilibrium the prevailing concentrations of the two cation-constituents are  $c_K$  or  $c_H$  and  $c_K + dc_K$  or  $c_H + dc_H$  and their transference-numbers are  $T_K$  and  $T_H$ , it is evident, when one faraday passes from the KCl solution to the HCl solution, that  $T_K$  mols of potassium-ion are transferred from the concentration  $c_K$  to the concentration  $c_K + dc_K$  and  $T_H$  mols of hydrogen-ion from  $c_H$  to  $c_H + dc_H$ . At the same time  $T_{CL}$  equivalents of chloride-ion are transferred in the opposite direction; but this need not be considered, since its concentration is uniform throughout the

whole solution. The free energy decrease  $-dF$  attending this transference is therefore given by the equation:

$$-dF = -RT \left( T_K \frac{dc_K}{c_K} + T_H \frac{dc_H}{c_H} \right).$$

A corresponding transference, attended by a corresponding free-energy decrease, takes place between each pair of adjoining infinitesimal layers throughout the whole boundary-portion. The total free-energy decrease, which is equal to the electrical work  $E_{LF}$  attending the passage of one faraday, is therefore equal to the integral of this expression, taken for the  $c_K$  term between the limits  $c_K = c$  and  $c_K = 0$  and for the  $c_H$  term between the corresponding limits  $c_H = 0$  and  $c_H = c$ . That is:

$$-\Delta F = E_{LF} = RT \int_0^c \left( T_K \frac{dc_K}{c_K} - T_H \frac{dc_H}{c_H} \right).$$

Now the transference-number of any ion-constituent, as indicated in Art. 73, is equal to the ratio of the product of its concentration by its conductance to the sum of the corresponding products for all the ion-constituents present. Hence, assuming complete or equal ionization for the two substances in all the solutions and constant ion-mobilities of the three ions up to the concentration  $c$ , the following expressions result:

$$T_K = \frac{c_K \Lambda_K}{c_K \Lambda_K + c_H \Lambda_H + c \Lambda_{Cl}} \quad T_H = \frac{c_H \Lambda_H}{c_K \Lambda_K + c_H \Lambda_H + c \Lambda_{Cl}}.$$

Replacing  $c_H$  in the first of these expressions by  $c - c_K$ , and  $c_K$  in the second of these expressions by  $c - c_H$ , substituting the resulting values of  $T_K$  and  $T_H$  in the above free-energy equation, carrying out the indicated integration, and simplifying the result by appropriate transformations, there is obtained the following equation, corresponding to equation (2) of Art. 157.

$$E_{LF} = RT \log \frac{\Lambda_K + \Lambda_{Cl}}{\Lambda_H + \Lambda_{Cl}}.$$

*Prob. 47. — Derivation of the Equation for the Liquid-Potential between Solutions with Two Solutes at the Same Concentrations. — Derive the equation just given by the method stated in the text.*

**159. Determination of Ion-Concentrations and of Equilibrium-Constants by Means of Electromotive Force Measurements.** — Measurements of electromotive force, interpreted with respect to the electrode-potentials involved, furnish an important means of deter-

mining ion-concentrations which are so small that they cannot be readily measured by other methods. The so determined ion-concentrations may be used for calculating the solubilities of very slightly soluble salts or the ionization-constants or other equilibrium-constants of chemical reactions, as shown in the following problems. Measurements of electromotive force similarly interpreted are frequently employed by physiologists for determining the hydrogen-ion concentration in blood and other animal fluids, and sometimes by chemical analysts for the titration of acids and bases, especially in cases where the color of the solution makes the use of indicators unreliable.

*Prob. 48. — Determination of Solubility.* — The electromotive force of the cell  $\text{Ag(s)} + \text{AgI(s)}, \text{KI(0.1 f.)}, \text{KNO}_3(0.1 \text{ f.}), \text{AgNO}_3(0.1 \text{ f.}), \text{Ag(s)}$  is 0.814 volt at  $25^\circ$ . Calculate the solubility of silver iodide in water at  $25^\circ$ .

*Prob. 49. — Determination of the Ionization-Constant of Water.* — Calculate the ionization-constant of water (Art. 104) at  $18^\circ$  from the fact that the electromotive force of the cell  $\text{H}_2(1 \text{ atm.}), \text{HCl(0.1 f.)}, \text{KCl(0.1 f.)}, \text{KOH(0.1 f.)}, \text{H}_2(1 \text{ atm.})$  is -0.653 volt at  $18^\circ$ .

*Prob. 50. — Determination of Complex-Constants.* — The electromotive force of the cell  $\text{Ag(s)}, \text{K}^+\text{Ag(CN)}_2^-(0.01 \text{ n.}) + \text{KCN(1 n.)}, \text{KCl(1 n.)}, \text{Hg}_2\text{Cl}_2(\text{s}) + \text{Hg(l)}$  is 0.83 volt at  $25^\circ$ . Calculate the dissociation-constant of the complex-ion  $\text{Ag(CN)}_2^-$  at  $25^\circ$ . Neglect the liquid-potential, which is small in this case. *Ans.*  $1.5 \times 10^{-21}$ .

*Prob. 51. — Determination of the Hydrolysis of Salts and the Ionization-Constants of Slightly Ionized Acids.* — When a solution 0.05 formal in  $\text{Na}_2\text{HPO}_4$  is saturated with hydrogen at 1 atm., when a platinum electrode is placed in it, and when the half-cell  $\text{HCl(0.01 f.)} + \text{NaCl(0.1 f.)}, \text{H}_2(1 \text{ atm.})$ , is brought into contact with it, the cell thus formed is found to have at  $18^\circ$  an electromotive force of 0.398 volt. Calculate the hydrolysis of the salt and the ionization-constant of  $\text{HPO}_4^-$ , assuming complete ionization of the largely ionized substances, and neglecting the liquid-potential, which is made small by the addition of the sodium chloride.

*Prob. 52. — Determination of Indicator-Constants.* — When the  $\text{Na}_2\text{HPO}_4$  solution of Prob. 51 is made 0.0001 formal in phenolphthalein the indicator is found to show a color 13% as intense as that which is produced on adding to the solution an excess of sodium hydroxide. Calculate the ionization-constant of this indicator.

*Prob. 53. — Electrometric Titration of Acids and Bases.* — Into a solution of an acid to be titrated are introduced the side-arm of a calomel half-cell and a tube carrying a small platinized platinum electrode, around which hydrogen gas at the barometric pressure is kept bubbling. A standard 0.5 n. NaOH solution is added from a burette until the electromotive force between the hydrogen electrode and the

calomel electrode is found to change very rapidly as more alkali is added. Calculate the successive changes that would be observed in the electromotive force, when the alkali added is equivalent to 99.0, 99.5, 99.8, and 100.2% of the acid present, *a*, in case the acid to be titrated is a 0.1 normal solution of HCl; *b*, in case it is a 0.1 normal solution of an acid of ionization-constant of  $10^{-5}$ , referring to the table of Art. 108 for the hydrogen-ion concentrations. Neglect the liquid-potential and the change in the volume of the solution produced by the addition of the standard NaOH solution.

## V. THE EQUILIBRIUM OF OXIDATION REACTIONS IN RELATION TO THE ELECTRODE-POTENTIALS

**160. Derivation of the Equilibrium-Constants of Oxidation Reactions from the Molal Electrode-Potentials.** — When the concentrations of the substances involved in the two electrode reactions of any cell are such that the two electrode-potentials are equal to each other, there is evidently no tendency for the cell to act nor for the chemical change to take place in it. In other words, the concentrations that make the two electrode-potentials equal are concentrations at which the chemical change is in equilibrium. The equilibrium-constant of a chemical change involving solutes or gases at small concentrations or pressures can therefore be evaluated, as in the following problems, by conceiving a cell in which the reaction would take place and calculating from the molal electrode-potentials by the usual logarithmic equation the concentrations of the substances involved in the electrode reaction that will make the two actual electrode-potentials equal.

*Evaluation of Equilibrium-Constants by a Consideration of the Equilibrium Conditions of Voltaic Cells.* —

*Prob. 54.* — *a.* Calculate the concentration of copper-ion at which the reaction  $\text{Zn(s)} + \text{Cu}^{++} = \text{Cu(s)} + \text{Zn}^{++}$  is in equilibrium at  $25^\circ$  when the zinc-ion is 1 molal. *b.* Calculate the equilibrium-constant at  $25^\circ$ .

*Prob. 55.* — *a.* Calculate the concentration of hydrogen-ion at which the reaction  $\text{Pb(s)} + 2\text{H}^+\text{Cl}^- = \text{H}_2(\text{g}) + \text{Pb}^{++}\text{Cl}_2^-$  is in equilibrium at  $25^\circ$  when the hydrogen has a pressure of 1 atm. and the lead-ion is 0.03 molal. *b.* Formulate an algebraic relation between the equilibrium-constant of the corresponding ion reaction and the molal electrode-potentials. *c.* Calculate the value of this equilibrium-constant.

The foregoing considerations evidently lead to a general expression for the equilibrium-constants of oxidation reactions. Namely, the equilibrium-constant  $K$  of the reaction which takes place when  $N$  faradays of electricity pass from left to right through a cell whose left-hand and right-hand molal electrode-potentials are  $\tilde{E}_1$  and  $\tilde{E}_2$ , respectively, is related to these potentials as follows:

$$RT \log K = (\tilde{E}_1 - \tilde{E}_2) NF.$$

This relation may be directly derived from free-energy considerations in the following way. The free-energy decrease attending a chemical reaction when the reacting substances and reaction-products are all at 1 molal (or if gaseous, at 1 atmosphere) has been shown in Arts. 140 and 141 to be given by the expression:

$$-\Delta F = RT \log K.$$

The free-energy decrease attending this same change in state, when this is considered to take place in a cell in which all the substances are at 1 molal (or if gaseous, at 1 atmosphere), is evidently expressed by the equation:

$$-\Delta F = nF (\tilde{E}_1 - \tilde{E}_2).$$

By equating these two expressions for the free-energy decrease the general relation given above obviously results.

It will be seen from these considerations that electrode-potentials are of great importance in their purely chemical relations. When they are so considered they are appropriately called the *reduction-potentials* of the corresponding oxidation reactions. Thus, the electrode-potential (0.122 volt) of  $\text{Pb(s)}$ ,  $\text{Pb}^{++}$  is the reduction-potential of the reaction  $\text{Pb(s)} + 2\oplus = \text{Pb}^{++}$ .

Expressed in chemical terminology, the preceding equation shows how the equilibrium-constant  $K$  of a chemical reaction which is the resultant of an oxidation reaction (such as  $\text{Pb(s)} + 2\oplus = \text{Pb}^{++}$ ) and of a reduction reaction (such as  $2\text{H}^+ = \text{H}_2(\text{g}) + 2\oplus$ ) is related to their molal reduction-potentials,  $\tilde{E}_1$  and  $\tilde{E}_2$ ; the symbol  $n$  denoting now the number of positive electrons involved in the separate reactions.

*Evaluation of Equilibrium-Constants by the General Equation. —*

*Prob. 56. — a.* Derive an expression for the equilibrium-constant of the reaction  $\text{Cu(s)} + \text{Cu}^{++} = 2\text{Cu}^+$  in terms of the molal reduction-potentials. *b.* Calculate the concentration of cuprous salt resulting when copper is shaken with a 0.1 f.  $\text{CuSO}_4$  solution at  $25^\circ$ . *c.* Calculate the concentration of cupric salt in the equilibrium-mixture produced by shaking a 0.1 f.  $\text{CuCl}_2$  solution with copper at  $25^\circ$ , noting that solid  $\text{CuCl}$  separates, whose solubility-product at  $25^\circ$  is  $1.2 \times 10^{-6}$  molal. *Ans. b,* 0.0024; *c,* 0.00172.

*Prob. 57. — a.* Formulate an algebraic expression showing how the equilibrium-constant of the reaction  $\text{Ag(s)} + \text{Fe}^{+++} = \text{Ag}^+ + \text{Fe}^{++}$ , expressed in terms of the equilibrium concentrations, is related to the molal reduction-potentials involved. *b.* Calculate the equilibrium-constant. *c.* Find the composition of the equilibrium mixture that results when metallic silver is placed in 0.1 f.  $\text{Fe(NO}_3)_3$  solution. *Ans. b,* 0.14; *c,*  $\text{Ag}^+$  or  $\text{Fe}^{++}$ , 0.067.

*Prob. 58. —* Manganates in aqueous solution undergo partial decomposition into permanganates and manganese dioxide according to the following equation:  $3\text{MnO}_4^- + 2\text{H}_2\text{O} = \text{MnO}_2(\text{s}) + 2\text{MnO}_4^- + 4\text{OH}^-$ . Calculate the ratio of permanganate to manganate in the equilibrium mixture at  $25^\circ$  when in that mixture the manganate is 0.1 formal and the free base is 1 formal. The molal reduction-potentials at  $25^\circ$  are  $-0.61$  volt for the reaction  $\text{MnO}_4^- + \oplus = \text{MnO}_4^-$ , and  $-0.66$  volt for the reaction  $\text{MnO}_2(\text{s}) + 4\text{OH} + 2\oplus = \text{MnO}_4^- + 2\text{H}_2\text{O}$ . *Ans. 2.21.*

## VI. VOLTAIC ACTION, ELECTROLYSIS, AND POLARIZATION

**161. Concentration-Changes Attending Voltaic Action and the Resulting Polarization.** — Throughout the foregoing considerations, as an aid in evaluating the electromotive force, it has been assumed that so large a quantity of solution is present in the cell that only infinitesimal concentration-changes are produced in it by the passage of a finite quantity of electricity. The fact that this is not the case in actual cells must be taken into account, as in the following problem.

*Prob. 59. — Change of Electromotive Force due to Changes in Concentration.* — The electromotive force  $E$  at  $15^\circ$  of the lead storage-cell varies with the mol-fraction  $x$  of the  $H_2SO_4$  (for values of  $x$  up to 0.10) according to the equation  $E = 1.855 + 3.80x - 10x^2$ . Out of a certain cell which contains 1300 g. of 10 mol-percent  $H_2SO_4$  a steady current of 5.36 amperes is taken for 10 hours. Calculate the electromotive force of the cell at the beginning and at the end.

In practice the electromotive force is often decreased much more than these considerations indicate because the concentration-changes actually occur in the immediate neighborhood of the electrodes and are only gradually distributed by convection or diffusion through the whole body of the solution. Thus in the lead storage-cell water is produced and acid is destroyed by the electrode reaction in the solution impregnating the porous lead-peroxide electrode, and the acid can only be replenished from the main body of the solution by the slow process of diffusion. This phenomenon is one kind of polarization, sometimes called *concentration-polarization*; the name *polarization* being used in general to denote the production by the passage of the current of any change in the solution adjoining the electrode or in the surface of the electrode which makes its potential deviate from its normal value.

Concentration-polarization is affected by various incidental conditions, for example, by agitation of the solution around the electrodes. It is also often greatly influenced by the *current-density*, by which is meant the current per unit-area of electrode surface, thus the number of amperes per square centimeter or square decimeter of surface of a specified electrode.

*Prob. 60. — Concentration-Polarization and the Factors Affecting It.* — When a current is taken at  $25^\circ$  out of a certain cell of the form  $Zn(s), ZnSO_4(1 f.), CuSO_4(1 f.), Cu(s)$ , the electromotive force soon becomes fairly constant and remains so for a time at a value 0.06 volt below its normal value. *a.* Show quantitatively how this might be

accounted for by concentration-polarization. *b.* Explain how the polarization would be affected by increasing the current; by using smaller electrodes without changing the current, thereby increasing the current-density; and by stirring the solutions, these being separated from each other by a porous cup.

### 162. Electrolysis in Relation to Minimum Decomposition-Potential.

— In order to produce electrolysis in any electrolytic cell there must obviously be applied from an external source an electromotive force at least equal to the electromotive force that is produced by the combination of solution and electrodes, considering it as a voltaic cell. The value of the electromotive force that must be applied to compensate the electromotive force of the voltaic cell which develops under the actual conditions, assuming local concentration changes to be equalized, may be called the *minimum decomposition-potential*. Its value can evidently be calculated in the case of cells with dilute solutions by the method considered in Art. 155. It is important to recognize this fact; for the decomposition-potential is sometimes treated as if it were an essentially independent quantity. The *actual decomposition-potential*, that is, the electromotive force that must be applied to produce continuous electrolysis, may be much greater than the minimum decomposition-potential because of polarization effects, such as are considered in the next article.

*Prob. 61. — Deposition of Metals by Electrolysis.* — A solution 0.05 formal in  $\text{H}_2\text{SO}_4$  and 0.05 formal in  $\text{CuSO}_4$  is electrolyzed at  $25^\circ$  between a mercury anode and a platinum cathode. In the mixture assume the salt to be completely ionized and the acid to be 25% ionized into  $2\text{H}^+$  and  $\text{SO}_4^{2-}$  and 75% ionized into  $\text{H}^+$  and  $\text{HSO}_4^-$ . *a.* Calculate from the molal electrode-potentials (taking that of  $\text{Hg(l)} + \text{Hg}_2\text{SO}_4\text{(s)}$ ,  $\text{SO}_4^{2-}$  to be  $-0.62$  volt) the minimum electromotive force which would have to be applied in order to cause the copper to deposit. *b.* Find the value to which this electromotive force would have to be increased after 99% of the copper had been precipitated in order that the deposition might continue, assuming the ionizations to be the same as in the original mixture. *c.* Find the minimum electromotive force at which hydrogen could be continuously set free, assuming that it attains at the cathode an effective pressure of 1 atm.

*Prob. 62. — Separation of Elements by Electrolysis.* — A solution 0.1 formal in  $\text{KCl}$ , 0.1 formal in  $\text{KBr}$ , and 0.1 formal in  $\text{KI}$  is placed, together with a platinum electrode, in a porous cup; and this is placed within a larger vessel containing a zinc electrode and a large quantity of 0.1 formal  $\text{ZnCl}_2$  solution. Neglecting the liquid-potential and any polarization effects, calculate the applied electromotive force required at  $25^\circ$ , *a.* to liberate 99.9% of the iodine; *b.* to set bromine free at a

concentration of 0.0001 molal; *c*, to liberate 99.9% of the bromine (which remains in solution); and *d*, to liberate chlorine at a concentration of 0.0001 molal.

**163. Electrolysis in Relation to Polarization.** — In electrolysis, as in voltaic action, concentration changes are produced in the solutions around the electrodes; and these changes have the effect of increasing the applied electromotive force required. Thus in electrolyzing a copper solution between copper electrodes (as is done in copper plating) only an infinitesimal electromotive force is required to start the deposition; but the solution around the cathode soon becomes less concentrated in copper and the solution around the anode more concentrated in copper, producing a concentration-cell with an electromotive force opposite to that applied. This back electromotive force would evidently be diminished by decreasing the current-density, by agitating the whole solution, or by rotating the electrodes.

When a gas, such as hydrogen or oxygen, is set free at an electrode, a phenomenon, known as *gas-polarization*, is observed which does not occur in the deposition of metals. For when a gas is involved in the electrode-reaction its partial pressure determines the electrode-potential. Hence in a cell exposed to the air a slow, continuous electrolysis may take place before the applied electromotive force equals the electromotive force of the cell when the gas-pressure is one atmosphere; for the gas-forming substance is produced on the electrode at a lower pressure and is dissolved in the solution and carried away by convection and diffusion. Moreover, a sudden increase in the rate of electrolysis does not take place when the applied electromotive force is increased beyond that corresponding to a pressure of one atmosphere; for the gas-forming substance then passes into the electrode at this higher pressure, producing a supersaturated adsorbed layer on its surface or a supersaturated solid solution within the metal, from which the gas does not escape rapidly enough to reduce the effective pressure to one atmosphere. There is thereby produced a *back electromotive force* which is equal to the electromotive force of a voltaic cell in which the gas has this higher pressure, and which is larger than the electromotive force of a similar cell in which the gas has the partial pressure that prevails above the solution. The amount by which the back electromotive force exceeds the theoretical electromotive force at the prevailing partial pressure is called the *polarization* or *overvoltage*.

It will thus be seen that the applied electromotive force may be considered resolved into three parts: one equal to the minimum decomposition-potential or to the theoretical electromotive force of the resulting voltaic cell at the prevailing partial pressures; a second part equal to the polarization; and a third part, that uncompensated by the back electromotive force resulting from these two effects, and therefore available for forcing a current through the cell in accordance with Ohm's law. These considerations are illustrated by Prob. 63.

These principles suffice to enable the phenomena of polarization to be treated from experimental and thermodynamic standpoints. The various hypotheses that have been proposed in regard to the molecular mechanism by which gas-polarization results can not be here considered. These hypotheses involve considerations relating to surface-tension, adsorption, formation of unstable compounds, and rate of reaction in solid phases.

The back electromotive force produced by the electrolysis may be experimentally determined in the following ways:

(1) By the method described in Prob. 63.

(2) By finding the smallest value of the applied electromotive force at which bubbles form slowly but continuously at the electrode surface (this giving a value corresponding practically to a minimum current-density).

(3) By applying a definite electromotive force to the cell long enough to charge the electrodes with the decomposition-products and then short-circuiting the electrodes through a high-resistance potentiometer, the applied potential being at the same time removed. From the so-measured back electromotive force the overvoltage is obtained by subtracting the theoretical electromotive force corresponding to the prevailing gas-pressure, which is usually about one atmosphere.

*Prob. 63. — Gas-Polarization.* — Electromotive forces successively increasing in magnitude were applied at 22° to an electrolytic cell consisting of a large, unpolarizable, platinized platinum plate as anode, a small mercury surface as cathode, and a 0.1 f.  $\text{H}_2\text{SO}_4$  solution as electrolyte. Hydrogen gas at 1 atm. was bubbled steadily through the cell, and a resistance of 100,000 ohms was placed in series with it, the resistance of the cell being negligible in comparison. The current-strengths in millionths of an ampere corresponding to various applied electromotive forces in volts were as follows:

Current-strength . . . .	0.06	0.44	1.20	2.20	3.70	4.82
Applied electromotive force .	0.32	0.48	0.62	0.77	0.95	1.08

*a.* Plot these current-strengths as ordinates against the electromotive forces as abscissas. *b.* Calculate the back electromotive force and polarization corresponding to each of these applied electromotive forces, tabulate these values, and plot the current-strengths against them on the same diagram. *c.* Calculate the effective pressure of the hydrogen at the electrode corresponding to the smallest of these back electromotive forces, assuming the logarithmic relation valid for perfect gases to hold up to this pressure.

The overvoltage is always found to increase with increase of the applied electromotive force and of the current-density; but it varies in a highly specific way with the chemical nature of the gas and with the chemical nature and physical state of the metallic electrode. Thus in certain experiments made with 1 normal  $\text{H}_2\text{SO}_4$  the overvoltage of the hydrogen was found to have the following values:

	Small current-density	Large current-density
Platinized platinum . . .	0.00 volt	0.07 volt
Smooth platinum . . . .	0.03	0.65
Lead . . . . .	0.36	1.23
Mercury . . . . .	0.44	1.30

In certain experiments with 2 normal KOH solution with a moderate current-density the overvoltage of the oxygen was found at the start to be 0.44 volt on platinized platinum, 0.84 volt on smooth platinum, and 0.50 volt on iron; the value increasing to 1.46 on smooth platinum and to 0.59 on iron after two hours' passage of the current.

The phenomenon of gas-polarization and the overvoltage attending it are of great significance in technical processes. The overvoltage may greatly diminish the energy-efficiency of the process, the *energy-efficiency* being the ratio of the minimum electrical energy theoretically required to produce a definite quantity of some product of the electrolysis to the energy actually expended. Overvoltage may also make processes practicable which would otherwise not be possible; thus in charging a lead storage-cell hydrogen is not set free at the lead owing to its overvoltage, although the potential of the half-cell  $\text{H}_2(1 \text{ atm.}), \text{H}_2\text{SO}_{4.20}\text{H}_2\text{O}$  is about 0.4 volt less than that of the half-cell  $\text{Pb} + \text{PbSO}_4(\text{s}), \text{H}_2\text{SO}_{4.20}\text{H}_2\text{O}$ .

*Prob. 64. — Energy-Efficiency and Overvoltage.* — In a certain commercial alkali-chlorine cell sodium hydroxide and chlorine are produced at an iron cathode and graphite anode, respectively, by the continuous electrolysis of a 25% NaCl solution which is slowly flowed through a diaphragm from the anode to the cathode compartment (to prevent the hydroxide-ion from migrating to the anode). In a certain case 4.5 volts

were applied to the cell, whose resistance was 0.00080 ohm, yielding a current of 2000 amperes; and there flowed off each hour from the cathode 27,460 g. of solution containing 10% of NaOH and 13% of NaCl. The electromotive force of the voltaic cell  $\text{H}_2(1 \text{ atm.})$ ,  $\text{NaOH}(10\%) + \text{NaCl}(13\%)$ ,  $\text{NaCl}(25\%)$ ,  $\text{Cl}_2(1 \text{ atm.})$  has been independently determined to be 2.3 volts. *a.* Calculate the current-efficiency in the production of the sodium hydroxide. *b.* Calculate the energy-efficiency of its production. *c.* Calculate the voltage used to produce the current and that used to overcome the polarization, and tabulate these together with the minimum decomposition-potential. *Ans. b, 47.0%.*

## CHAPTER XII

### THE EFFECT OF TEMPERATURE ON THE WORK PRODUCIBLE BY ISOTHERMAL CHEMICAL CHANGES AND ON THEIR EQUILIBRIUM CONDITIONS

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#### I. THE FUNDAMENTAL SECOND-LAW EQUATION

**164. The Quantity of Work Producing from a Quantity of Heat that Passes from One Temperature to Another.** — This chapter is mainly devoted to a consideration of the effect of temperature on the free-energy changes that attend isothermal changes in state. To this effect is closely related, in virtue of the free-energy relations already derived, the effects of temperature on the equilibrium of chemical changes and on the electromotive force of voltaic cells. Before these effects can be properly considered the more general thermodynamic relation referred to in the title of this article must be known. This will now be derived.

The second law of thermodynamics has already been expressed (in Art. 135) in fundamental form by the statement that a process whose final result is only a transformation of heat into work is an impossibility; and it was shown that, in accordance with this statement, when work is produced in surroundings of constant temperature, there is always a change in the state of the system employed for the transformation. Chapters X and XI have been devoted to a determination of the quantities of work producible by various isothermal changes in state. There will now be considered the other conditions, involving difference in temperature in the surroundings, under which the second law permits that work be produced out of heat by systems which undergo no permanent change in state.

When a quantity of heat is transformed into work by a *cyclical process* (that is, by a process in which the system undergoes a cycle of changes in state), an additional quantity of heat is always taken up from surroundings at a higher temperature and given out to surroundings at a lower temperature. That is to say, even when a difference of temperature exists, only a fraction of the heat taken up by the system from the warmer surroundings can be transformed into work. Important questions at once arise as to what determines the fraction that can be so transformed — whether it is dependent on the nature of the process employed, and how it varies with the temperatures.

In order to determine whether the quantity of work that can be produced when any definite quantity of heat is transferred by a cyclical process from a higher to a lower temperature is dependent upon the nature of the system employed for the transformation, or upon the way in which the transformation is carried out, assume that two different reversible cyclical processes, carried out with different systems or in a different way with the same system, could produce two unequal quantities of work by transferring an equal quantity of heat from a higher to a lower temperature. Then cause the process that produces the larger quantity of work  $W''$  to take place in such a way that it takes up a quantity of heat  $Q_1$  at the higher temperature  $T_1$ , transfers a part of it  $Q_2$  to the lower temperature  $T_2$ , and transforms the remainder into work  $W''$ ; and cause the other process, which in transferring the same quantity of heat  $Q_2$  from  $T_1$  to  $T_2$  produces the smaller amount of work  $W'$ , to take place in the reverse direction — that is, so that it takes up the heat  $Q_2$  transferred by the former process to the lower temperature, and raises it to the higher temperature by expending the required amount of work  $W'$ . It is then evident that the net result of these operations would be the production of a quantity of work  $W'' - W'$  from an equivalent quantity of heat without any other change having been brought about either in the systems or in the surroundings. Since this is contrary to the fundamental statement of the second law, the supposition made that the two processes produce unequal quantities of work is untenable. This important conclusion may be explicitly stated as follows: the quantity of work which can be produced when a definite quantity of heat is transferred from one temperature to another by any process in which the system employed undergoes no permanent change in state is not dependent on the nature of the process.

By the conclusion just reached the determination of the relation between the temperatures and the proportion of heat transformable into work is greatly facilitated; for evidently it is now only necessary to determine what that relation is for a single reversible cyclical process. Such a process is considered in the following problem.

*Prob. 1. — Derivation of the Second-Law Equation.* — Consider the following cyclical process carried out reversibly with  $N$  mols of a perfect gas contained in a cylinder closed with a weighted, frictionless piston. Start with the gas at the temperature  $T + dT$  and volume  $v_1$ . (1) Keeping the gas in a large heat-reservoir at  $T + dT$ , diminish gradually the weight on the piston and cause the gas to expand till its volume

becomes  $v_2$ . (2) Fix the piston so that the volume must remain constant, and place the gas in a large heat-reservoir at a temperature  $T$ . (3) Keeping the gas in the heat-reservoir at the temperature  $T$ , compress it by releasing the piston and gradually increasing the weight upon it until the volume  $v_2$  of the gas has been restored to its original value  $v_1$ . (4) Fix the piston again so as to keep the volume constant, and place the gas in a heat-reservoir at the temperature  $T+dT$ . *a.* Represent this process by a lettered diagram in which the ordinates denote temperatures and the abscissas volumes. *b.* Formulate an expression for the quantities of work  $W_1, W_2, W_3, W_4$ , and for the quantities of heat  $Q_1, Q_2, Q_3, Q_4$ , produced in the surroundings in the separate steps of this process, taking into account the principles considered in Arts. 24, 25, and 26. *c.* Formulate a relation between the quantity of work  $\Sigma W$  produced in the whole process and the quantity of heat  $Q$  imparted to the reservoir at the temperature  $T$ .

Since it was previously shown that the second law requires that the same quantity of work be produced when a definite quantity of heat is transferred by any reversible cyclical process whatever from one definite temperature to another, it is evident that the equation derived in the preceding problem for one such process is an exact expression of the second law for every such process. This equation therefore expresses one of the fundamental principles of physical science.

The equation just derived, which will be called simply the *second-law equation*, may be written in the form:

$$\Sigma W = Q \frac{dT}{T}.$$

In this equation  $\Sigma W$  denotes the algebraic sum of all the quantities of work produced in any reversible cyclical process taking place at two temperatures  $T$  and  $T+dT$  in which the quantity of heat  $Q$  is transferred to the surroundings at the temperature  $T$ . The work-quantity  $\Sigma W$  is obviously infinitesimal in correspondence with the infinitesimal temperature-difference  $dT$ .

*Prob. 2. — General Principles Deduced from the Second-Law Equation.* — Show that the second-law equation leads to the following conclusions: *a.* When there is no difference of temperature in the surroundings heat cannot be transformed at all into work by any cyclical process. *b.* In order to carry heat from a lower to a higher temperature work must be withdrawn from the surroundings. *c.* The fraction of the heat transformable into work for a given difference in temperature is greater the lower the temperature. *d.* When the lower temperature is the absolute zero heat can be completely transformed into work.

## II. THE EFFECT OF TEMPERATURE ON THE EQUILIBRIUM OF UNIVARIANT SYSTEMS

**165. Effect of Temperature on the Pressure at which the Phases of Univariant Systems are in Equilibrium.** — An important relation derivable from the second law of thermodynamics is that named in the title of this article. It is expressed by the *Clapeyron equation*:

$$\frac{dp}{dT} = \frac{1}{T} \frac{\Delta H}{\Delta v}.$$

In this equation  $dp$  denotes the increase produced by a temperature-increase  $dT$  in the pressure at which the phases of a univariant system are in equilibrium at the temperature  $T$ , and  $\Delta H$  and  $\Delta v$  denote the increases in heat-content and in volume which attend the conversion at the temperature  $T$  and at the equilibrium-pressure  $p$  of any definite quantity of substance from the state in which it exists in one phase or set of phases into the state in which it exists in the other phase or set of phases. For example, the temperature-coefficient  $dp/dT$  of the dissociation-pressure  $p$  of solid calcium carbonate at any temperature  $T$  can be calculated by substituting in the Clapeyron equation for  $\Delta H$  the increases in heat-content and for  $\Delta v$  the increase in volume that attend the change in state  $\text{CaCO}_3(\text{s}) = \text{CaO}(\text{s}) + \text{CO}_2(\text{at } p)$  at the temperature  $T$ .

This equation will now be derived from the second-law equation.

*Prob. 3. — Derivation of the Clapeyron Equation.* — Consider the following cyclical process: Start with some definite quantity of a substance (for example,  $1\text{H}_2\text{O}$ ) existing as a phase (for example, liquid water) which is in equilibrium with a second phase (for example, ice) at the temperature  $T$  and pressure  $p$ . (1) Cause the substance to pass under these equilibrium conditions from the first phase (liquid water) in which its volume is  $v_1$  into the second phase (ice) in which its volume is  $v_2$ ; (2) heat the substance to  $T+dT$ , whereby the pressure becomes  $p+dp$  and the volume  $v_2+dv_2$ ; (3) cause it to pass from the second phase (ice) into the first phase (liquid water) at  $T+dT$  under the equilibrium pressure  $p+dp$ , whereby the volume becomes  $v_1+dv_1$ ; (4) cool the substance to  $T$ , whereby it reverts to its original state. *a.* Represent this process by a diagram in which the ordinates denote pressures and the abscissas volumes. *b.* Formulate the quantities of work,  $W_1, W_2, W_3, W_4$ , produced in the four steps of the process when it is carried out reversibly, summate these quantities of work, cancel the differentials of the second order, substitute the result in the second-law equation, and replace the heat quantity  $Q$  in the equation by its equivalent  $-\Delta H$ . *c.* Specify the change in state to which the heat-content decrease  $-\Delta H$  refers.

In applications of the Clapeyron equation a definite change in state should first be formulated, and then  $\Delta H$  and  $\Delta v$  should be evaluated in accordance with it, expressing the heat-quantity  $\Delta H$  and the work-quantity  $dp \cdot \Delta v$  in the same units. When one of the phases involved is a gas at small pressure,  $\Delta v$  may be determined by neglecting the volume of the solid or liquid phases and expressing the volume of the gaseous phase in terms of its temperature and pressure with the aid of the perfect-gas law. Applications of the equation to systems of this kind (those involving liquid and gaseous phases) were considered in Art. 33. Other applications are illustrated by the following problems.

*Effect of Pressure on Melting Point. —*

*Prob. 4.* — Derive from the Clapeyron equation a principle expressing the direction of the effect of pressure on the melting-point of solid substances, taking into account the fact that fusion is always attended by an absorption of heat.

*Prob. 5.* — Calculate the variation per atmosphere of the melting-point of ice. At  $0^\circ$  and 1 atm. its density is 0.917 and the heat of fusion of 1 g. is 79.7 cal.

*Prob. 6.* — *Effect of Pressure on Transition-Temperature.* — *a.* Calculate the variation per atmosphere of the transition-temperature ( $95.5^\circ$ ) of rhombic into monoclinic sulfur from the densities of the two forms, which are 2.07 and 1.96 respectively, and from the fact that the transition of 1 at. wt. of sulfur from the rhombic into the monoclinic form is attended at  $95.5^\circ$  by an absorption of 105 cal. *b.* State what this shows as to the slope of the line BE in the sulfur diagram of Art. 115; and what conclusion as to the slope of the line CF can be drawn by considering the density of liquid sulfur, which is 1.81 at  $115^\circ$ .

*Prob. 7.* — *Heat of Hydration derived from the Vapor-Pressure of Salt-Hydrates.* — With the aid of the temperature-vapor-pressure curves of the diagram of Art. 120 derive approximate values of the heat-effect attending the reaction  $\text{Na}_2\text{HPO}_4 \cdot 7\text{H}_2\text{O}(s) + 5\text{H}_2\text{O}(g) = \text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}(s)$  at  $25^\circ$ .

In order to integrate the Clapeyron equation exactly,  $\Delta H$  and  $\Delta v$  must be expressed as functions either of the equilibrium-temperature or of the equilibrium-pressure. When the system consists of only solid and liquid phases and when only moderate changes of pressure (such as 20 atm.) are involved,  $\Delta H$ ,  $\Delta v$ , and  $T$  in the second member of the equation may be considered constant in approximate calculations. When one of the phases consists of a perfect gas,  $\Delta v$  may be expressed as a temperature-function by means of the perfect-gas equation. The heat-quantity  $\Delta H$  may always be so expressed in terms of the heat-capacities of the substances involved, in the way described in Art. 131.

*Applications of Integrated Forms of the Clapeyron Equation. —*

*Prob. 8.* — Calculate the melting-point of ice at 20 atm. with the aid of the data of Prob. 5.

*Prob. 9.* — State what heat-quantity can be calculated from the dissociation-pressures of solid  $\text{NH}_4\text{SH}$  into  $\text{NH}_3$  and  $\text{H}_2\text{S}$ , which are 500 mm. at  $25^\circ$  and 182 mm. at  $10^\circ$ ; and calculate its value, assuming it to be constant through the temperature interval involved.

*\*Prob. 10.* — Calculate the vapor-pressure of solid iodine at  $25^\circ$  from the following data: Its vapor-pressure at  $100^\circ$  is 47.5 mm., its molal heat of vaporization at  $100^\circ$  is  $-14,600$  cal., its atomic heat-capacity is 6.7 between  $25^\circ$  and  $100^\circ$ , and the molal heat-capacity of its vapor at constant pressure is 7.8 between those temperatures.

\*The derivation of the Clapeyron equation shows that it determines the equilibrium conditions of any type of system in which an isothermal change in state can take place under a constant equilibrium-pressure, which is determined only by the temperature; for evidently in all such cases, and only in such cases, the expressions for the work-quantities involved in the cyclical process by which the equation was derived will have the same form. An isothermal change can, however, take place without any change in the pressure only when the pressure is determined solely by the temperature and is not changed by any transfer of substance from one phase of the system to another. In other words, the Clapeyron equation is applicable to all systems, and only to systems, which are actually or in effect univariant. Thus it has been shown applicable to one-component systems existing in two phases, like ice and water or water and water-vapor, or to two-component systems existing in three phases, like  $\text{CaCO}_3$ ,  $\text{CaO}$ , and  $\text{CO}_2$ . It is also applicable, however, to systems that have been made in effect univariant by the specification that the composition of each of the phases present shall remain constant when the isothermal change takes place and when the temperature of the system is varied. Thus the equation can be applied to a two-component system existing in only two phases, like a solution and its vapor, provided such a change in state be considered that the solution remain constant in composition when some of the solvent vaporizes out of it, as in the case when an infinite quantity of the solution is subjected to the process. Hence the equation can be used to determine the change in the vapor-pressure of a solution with the temperature. Similarly, it can be applied to a two-component system consisting of a solution and a solid phase, like a melted binary alloy in contact with one of the solid

metals, so as to determine the effect of pressure on the temperature at which the solid metal will separate from a melt of the specified composition.

*\*Prob. 11. — Application of the Clapeyron Equation to Solutions. —*

- a.* In applying the Clapeyron equation to determine the effect of temperature on the vapor-pressure of a 10% NaCl solution, specify the change in state to which the quantities  $\Delta H$  and  $\Delta v$  would correspond.
- b.* State what equilibrium could be studied by applying the Clapeyron equation to a system consisting of solid sodium chloride and its saturated solution, and specify the change in state to which the quantities  $\Delta H$  and  $\Delta v$  would correspond.

## III. THE EFFECT OF TEMPERATURE ON THE EQUILIBRIUM OF CHEMICAL REACTIONS IN GENERAL

**166. The Effect of Temperature on the Free-Energy Decrease Attending Any Isothermal Change in State.** — By applying the fundamental second-law equation to certain reversible cyclical processes there can be derived, as shown in Probs. 12 and 13, the following differential equations expressing the change with the temperature of the decreases  $-\Delta A$  and  $-\Delta F$ , defined as in Art. 136, in the work-content and in the free energy of a system attending any isothermal change in its state.

$$\frac{d(-\Delta A)}{dT} = \frac{\Delta U - \Delta A}{T}. \quad (1)$$

$$\frac{d(-\Delta F)}{dT} = \frac{\Delta H - \Delta F}{T}. \quad (2)$$

These equations are general expressions of the second law in forms especially convenient in considerations relating to chemical equilibrium and electromotive force. It is important fully to appreciate the significance of the quantities occurring in them and the case to which each equation is applicable. These are shown by the derivations of the equations (in Probs. 12 and 13) to be as follows. The quantities  $-\Delta A$  and  $-\Delta F$  denote the decreases in the work-content and in the free energy of the system which attend any isothermal change in its state at the temperature  $T$ ; and  $\Delta U$  and  $\Delta H$  denote the accompanying increases in its energy-content and heat-content. The differential quantities  $d(-\Delta A)$  and  $d(-\Delta F)$  signify that when the same change in state takes place at  $T + dT$ , instead of at  $T$ , it is attended by a work-content decrease of  $-\Delta A + d(-\Delta A)$  and by a free-energy decrease of  $-\Delta F + d(-\Delta F)$ , instead of one of  $-\Delta A$  and of  $-\Delta F$ . The work-content equation is applicable to cases where the initial volume, and also the final volume, of the system is the same at the two temperatures; and the free-energy equation is applicable to cases where the initial pressure, and also the final pressure, is the same at the two temperatures.

In accordance with the practice adopted throughout the preceding considerations, only the free-energy equation will hereafter be employed. For purposes of integration this equation is more conveniently written in the following forms:

$$d\left(\frac{-\Delta F}{T}\right) = \frac{\Delta H}{T^2} dT. \quad (3)$$

$$\frac{-\Delta F_2}{T_2} - \frac{-\Delta F_1}{T_1} = \int_{T_1}^{T_2} \frac{\Delta H}{T^2} dT. \quad (4)$$

This equation in any of its forms will be called the *second-law free-energy equation*.

*Derivation of the Work-Content and Free-Energy Equations. —*

*Prob. 12.* — To derive equation (1) given in the above text, consider a reversible cyclical process involving the following steps: (1) Any change in state of any system at the temperature  $T$ , by which a quantity of work  $W$  is produced; (2) a change in the temperature of the system at constant volume from  $T$  to  $T+dT$ ; (3) a change in the state of the system at the temperature  $T+dT$  which is the reverse of the change in state in the first step, this change being attended by a production of a quantity of work  $-(W+dW)$ ; (4) a change in the temperature of the system at constant volume from  $T+dT$  to  $T$ . *a.* Represent this process by a lettered diagram in which the ordinates denote temperatures and the abscissas volumes. *b.* Find an expression for  $\Sigma W$  for this process. *c.* By substituting it in the second-law equation and by making other appropriate substitutions, show that equation (1) results.

*Prob. 13.* — To derive equation (2) given in the above text, consider a reversible cyclical process just like that described in the preceding problem, except that in steps (2) and (4) the system is kept at constant pressure, instead of at constant volume. *a.* Represent this process by a lettered diagram in which the ordinates denote temperatures and the abscissas volumes, designating the pressures and volumes of the system at the beginning of each of the four steps by (1)  $p_1$  and  $v_1$ ; (2)  $p_2$  and  $v_2$ ; (3)  $p_2$  and  $v_2+dv_2$ ; and (4)  $p_1$  and  $v_1+dv_1$ . *b.* Find an expression for  $\Sigma W$  for this process. *c.* By substituting this expression in the second-law equation and making other appropriate substitutions based on the definitions of  $-\Delta F$  and  $-\Delta H$  given in Arts. 136 and 128, show that equation (2) results. *d.* Show that the free energy equations (2) and (3) are identical by carrying out in the first member of equation (3) the indicated differentiation and by making simple transformations.

**167. The Effect of Temperature on the Equilibrium of Chemical Changes Involving Perfect Gases.** — By substituting in the second-law free-energy equation (3) of Art. 166 the expression derived in Arts. 140 and 142 for the free-energy decrease attending an isothermal chemical change between perfect gases or between solid substances and perfect gases, and noting that the initial and final pressures occurring in this expression must not vary with the temperature if this equation (3) is to be applicable, there is obtained the following equation, commonly called the *van't Hoff equation*, expressing the effect of tempera-

ture on the equilibrium pressures  $p_A$ ,  $p_B$ , etc., and on the equilibrium-constant  $K$  of the chemical reaction:

$$d \log \frac{p_E^e p_F^f \dots}{p_A^a p_B^b \dots} = d \log K = \frac{\Delta H}{RT^2} dT.$$

*Prob. 14. — Derivation of the Van't Hoff Equation.* — Derive in the way indicated in the text the van't Hoff equation from the general expression given in Art. 140 for the free-energy decrease attending any chemical change between gases.

*Prob. 15. — Qualitative Principle Expressing the Effect of Temperature on Chemical Equilibrium.* — Derive from the van't Hoff equation a principle showing how the direction in which an equilibrium is displaced by increase in temperature is related to the sign of the heat-effect attending the reaction.

*Applications of the Qualitative Principle.* —

*Prob. 16.* — Show how the equilibrium in a gaseous mixture of  $\text{Cl}_2$ ,  $\text{HCl}$ ,  $\text{O}_2$ , and  $\text{H}_2\text{O}$  at  $25^\circ$  would be displaced by increasing the temperature. The heat of formation at  $25^\circ$  of  $\text{HCl(g)}$  is 22,000 cal. and that of  $\text{H}_2\text{O(g)}$  is 57,800 cal.

*Prob. 17.* — The dissociation-pressure of solid  $\text{CaCO}_3$  (and of all other solid substances which dissociate into one or more gaseous products) increases with rising temperature. State whether heat is absorbed or evolved when the dissociation takes place at constant temperature.

In order to integrate the van't Hoff equation, the heat-content increase  $\Delta H$  must be expressed as a function of the temperature.

This temperature function is usually derived, in the way shown in Art. 131, from a knowledge of the heat-content increase at some one temperature and of the heat-capacities at constant pressure of the substances involved in the reaction. Thus the function may always be obtained by integrating the following differential equation, in which  $\Delta C$  represents the difference between the heat-capacity (equal to  $C_E + C_F \dots$ ) of the system in its final state and its heat-capacity (equal to  $C_A + C_B \dots$ ) in its initial state:

$$d(\Delta H) = \Delta C.dT.$$

The integration can evidently be carried out when  $\Delta C$  is known to be constant or when it can be expressed as a function of the temperature, as illustrated by the following problems.

*Integration of the Van't Hoff Equation.* —

*Prob. 18.* — *a.* Derive the expression  $d(\Delta H) = \Delta C.dT$  in the way described in Art. 131. *b.* Integrate it for the case that  $\Delta C$  is a function of the form  $\Delta C = \Delta C_0 + \alpha T + \beta T^2$ , where  $\Delta C_0$ ,  $\alpha$ , and  $\beta$  are constants.

*Prob. 19.* — Find a numerical expression for  $\Delta H$  for the reaction

$2\text{CO(g)} + \text{O}_2\text{(g)} = 2\text{CO}_2\text{(g)}$  from the heat-capacity data given in Art. 27 and in Prob. 29 of Art. 134 and the heats of formation of  $\text{CO(g)}$  and  $\text{CO}_2\text{(g)}$  at  $20^\circ$ , which are 25,900 and 94,200, respectively.

*Prob. 20.* — Integrate the van't Hoff equation between the limits  $T_1$  and  $T_2$ ,  $K_1$  and  $K_2$ , for the following cases: *a*, when  $\Delta C$  is zero and therefore  $\Delta H$  does not vary with the temperature; *b*, when  $\Delta C$  has a finite value which does not vary with the temperature; *c*, when  $\Delta C$  varies with the temperature in the way considered in Prob. 18*b*.

In numerical applications of the van't Hoff equation, in order to guard against errors in the sign of the heat-content increase and in its value with respect to the multiple chosen, the reaction under consideration should first be formulated in a definite chemical equation and then values of  $K$ ,  $\Delta H$ , and  $\Delta C$  should be adopted in conformity with it. For the heat-capacities of some important gaseous substances and of elementary solid substances see Arts. 27 and 55.

*Applications of the Van't Hoff Equation to the Equilibrium of Gas Reactions.* —

*Prob. 21.* — It has been found that when dry air (containing 21.0 mol-percent of oxygen and 78.0 mol-percent of nitrogen) is kept at  $1957^\circ$  till equilibrium is reached, 4.3% of the oxygen present is converted into nitric oxide. Calculate the percentage that would be so converted at  $3000^\circ$ . The formation of  $\text{NO(g)}$  from its elements at  $20^\circ$  is attended by a heat-absorption of 21,600 cal. For the heat-capacities of the three gases see Art. 27. *Ans.* 18.5%.

*Prob. 22.* — Formulate an exact numerical expression by which the dissociation  $\gamma$  of carbon dioxide into carbon monoxide and oxygen at any temperature  $T$  and any total pressure  $p$  can be calculated. Its dissociation at  $1205^\circ$  and 1 atm. is 0.032%. Refer to Prob. 19 for the heat data needed.

*Prob. 23.* — When a mixture of 0.49 mol of  $\text{O}_2$  and 1.00 mol of  $\text{HCl}$  is kept at  $386^\circ$  and 1 atm. in contact with solid cuprous chloride (which acts as a catalyst) till equilibrium is reached, 80% of the  $\text{HCl}$  is converted into  $\text{Cl}_2$  and  $\text{H}_2\text{O}$ . *a*. Formulate the reaction, and calculate its equilibrium-constant at  $386^\circ$ . *b*. Formulate as a function of the absolute temperature the increase in heat-content attending this reaction, using the heat-content data of Prob. 16 and the heat-capacity data of Art. 27 and of Prob. 17, Art. 131. *c*. Derive from these results a numerical expression for the equilibrium-constant at  $25^\circ$ .

*Prob. 24.* — Calculate from the heat data given below and the values of the heat-capacities given in Art. 27: *a*, the heat of dissociation of  $\text{HgO(s)}$  into mercury vapor and oxygen at  $357^\circ$ ; *b*, a temperature-function expressing the heat-content increase attending this dissociation above  $357^\circ$ ; *c*, the dissociation-pressure of solid mercuric oxide at  $357^\circ$ . The heat of formation of  $\text{HgO(s)}$  at  $20^\circ$  is 21,700 cal.

The vaporization of  $\text{rHg(l)}$  at its boiling-point ( $357^\circ$ ) absorbs 14,160 cal. The mean value of the atomic heat-capacity of liquid mercury between  $20^\circ$  and  $357^\circ$  is 6.36 cal. per degree; and the heat-capacity of  $\text{rHgO(s)}$  may be taken as 10.87 at all temperatures. The dissociation-pressure of mercuric oxide at  $390^\circ$  is 180 mm. *Ans. a, 35,500 cal.; c, 70 mm.*

**168. The Effect of Temperature on the Equilibrium of Chemical Changes Involving Perfect Solutes.**—By substituting in the second-law free-energy equation of Art. 166 the expression given in Art. 141 for the free-energy decrease attending any chemical change between perfect solutes, and noting that in that expression the last term containing the initial and final molalities does not vary with the temperature when the solution is heated at constant pressure, there again results the van't Hoff equation, now expressed in terms of the equilibrium molalities:

$$d \log \frac{c_E^e c_F^f \dots}{c_A^a c_B^b \dots} = d \log K = \frac{\Delta H}{RT^2} dT.$$

This equation is applicable also to chemical changes between solid substances and solutes at small concentrations, since it was shown in Art. 142 that the participation of solid substances in the change does not affect the expression for the free energy. It applies also to changes in which the solvent (thus the water in aqueous solutions) enters into reaction with solutes at small concentrations.

From this equation, as from the corresponding one in terms of pressures, can be derived the important qualitative principle that the equilibrium of a chemical change is displaced by increase of temperature in that direction in which the reaction is attended by an increase in heat-content (or by an absorption of heat).

The integration of the equation evidently involves the expression of the heat-content as a function of the temperature. Since in the case of solutions the temperature interval often is not large, the increase in heat-content can frequently be regarded as constant; and it is to be so regarded in the following problems unless otherwise stated. When this is not admissible its variation with the temperature must be known. This must usually be derived from direct determinations of the heat-effects attending the reaction at two or more different temperatures; for there is likely to be a large error involved in calculating it from the partial heat-capacities of the solutes, since they form only a small part of the total heat-capacity of the solution.

*Prob. 25. — Application of the Qualitative Principle.* — State the conclusions in regard to the heat of solution that can be drawn from the facts that solubility of all gaseous substances is decreased, and the solubility of most solid substances is increased, by an increase of temperature.

*Prob. 26. — Effect of Temperature on the Ionization of Water.* — The neutralization of largely ionized univalent acids and bases in fairly dilute solution has been found by direct measurements at  $2^{\circ}$ ,  $10^{\circ}$ ,  $18^{\circ}$ ,  $26^{\circ}$ , and  $34^{\circ}$  to evolve 14,750 — 52 cal. at the centigrade temperature  $t$ . The value of the ionization-constant of water at  $25^{\circ}$  is  $1.00 \times 10^{-14}$ . Calculate its value at  $0^{\circ}$ . *Ans.*  $0.1 \times 10^{-14}$ .

*Prob. 27. — Effect of Temperature on the Hydrolysis of Salts.* — Calculate the hydrolysis of 0.1 f.  $\text{NH}_4\text{CN}$  at  $0^{\circ}$  from its hydrolysis (47%) at  $25^{\circ}$  and from the fact that on mixing at  $25^{\circ}$  a solution containing 0.2  $\text{NH}_3$  and 1000 g. of water with one containing 0.2  $\text{HCN}$  and 1000 g. of water and bringing the mixture back to  $25^{\circ}$  there is a heat evolution of 152 cal.

*Prob. 28. — Effect of Temperature on Solubility.* — The solubility of silver chloride in water is  $1.10 \times 10^{-5}$  formal at  $20^{\circ}$  and  $15.2 \times 10^{-5}$  formal at  $100^{\circ}$ . *a.* State just what heat-quantity can be computed from these data, and calculate its value. *b.* State by what thermochemical measurement it could be determined experimentally.

## IV. THE EFFECT OF TEMPERATURE ON THE ELECTROMOTIVE FORCE OF VOLTAIC CELLS

**169. The Effect of Temperature on the Electromotive Force of Voltaic Cells.** — By substituting in the second-law free-energy equations of Art 166 the quantity  $E_{NF}$  shown in Art 145 to represent the free-energy decrease attending any change in state taking place reversibly in a voltaic cell there result the following expressions, known as the *Gibbs-Helmholtz equation*, for the effect of temperature on the electromotive force of voltaic cells:

$$NF \frac{dE}{dT} = \frac{\Delta H + E_{NF}}{T}; \text{ or } NF d\left(\frac{E}{T}\right) = \frac{\Delta H}{T^2} dT.$$

In this equation  $\Delta H$  denotes the increase in heat-content which attends the change in state that takes place when  $N$  faradays of electricity flow through a cell of electromotive force  $E$  containing infinite quantities of the constituent substances.

*Effect of Temperature on Electromotive Force.* —

*Prob. 29.* — Show from the Gibbs-Helmholtz equation under what conditions the electromotive force of a cell,  $a$ , is independent of the temperature;  $b$ , is proportional to the absolute temperature;  $c$ , increases with rising temperature;  $d$ , decreases with rising temperature.

*Prob. 30.* —  $a$ . Calculate the temperature-coefficient at  $25^\circ$  of the electromotive force of the cell  $H_2(1 \text{ atm.}), H_2SO_4(0.01 \text{ f.}), O_2(1 \text{ atm.})$ , which was found in Prob. 20, Art. 149, to be 1.228 volts.  $b$ . Calculate the electromotive force of this cell at  $0^\circ$ , assuming that the heat-effect attending the change in state does not vary appreciably between  $0$  and  $25^\circ$ .

*Prob. 31.* — Calculate the temperature-coefficient at  $25^\circ$  of the electromotive force (1.262 volts) of the cell  $H_2(1 \text{ atm.}), HCl(4 \text{ f.}), Cl_2(1 \text{ atm.})$  from the heat-content ( $-22,000 \text{ cal.}$ ) of  $1HCl(g)$  and its heat of solution ( $16,000 \text{ cal.}$ ) in 4 f.  $HCl$  solution.

*Prob. 32.* — Calculate the electromotive force at  $40^\circ$  of the storage-cell  $Pb(s) + PbSO_4(s), H_2SO_4.10H_2O, PbSO_4(s) + PbO_2(s)$ , from its electromotive force (2.096 volts) at  $0^\circ$  and the heat data needed. The heat-contents at  $18^\circ$  of  $1PbSO_4(s), 1PbO_2(s)$ , and  $1H_2SO_4(l)$  are  $-216,210 \text{ cal.}, -62,900 \text{ cal.},$  and  $-192,900 \text{ cal.},$  respectively. The heats of solution at  $18^\circ$  of  $1H_2SO_4(l)$  and of  $1H_2O(l)$  in  $H_2SO_4.10H_2O$  are  $12,820 \text{ cal.}$  and  $230 \text{ cal.},$  respectively.

*Prob. 33.* — *Calculation of Heat of Reaction.* — The electromotive force of the cell  $Hg(l) + Hg_2Cl_2(s), KCl(0.01 \text{ f.}) + KNO_3(1 \text{ f.}), KNO_3(1 \text{ f.}) + KOH(0.01 \text{ f.}), Hg_2O(s) + Hg(l)$  at  $0^\circ$  is 0.1483 volt and at  $18.5^\circ$  is 0.1636 volt.  $a$ . Formulate the change in state that takes place in the cell when two faradays pass through it.  $b$ . Calculate the attendant increase in its heat-content.

\*It will have been noted that the calculation of the increase in heat-content attending chemical changes in voltaic cells involves the heat-effect produced by the addition of definite quantities of the solute or solvent to an infinite quantity of the solution at a specified concentration. This kind of heat-effect often has to be considered also in evaluating the increase in heat-content used in calculating the change with the temperature of the equilibrium conditions of chemical systems, as in the application of the Clapeyron equation to solutions in Art. 165. It is called (because of the relation derived in Prob. 35*b*) the *partial heat of solution* of the substance. It can be derived from calorimetrically measured heats of dilution, like those considered in Art. 132, in the ways illustrated by the following problems.

*\*Determination of Partial Heats of Solution. —*

*\*Prob. 34. —* The measured heat-effect  $Q$  attending the mixing of  $1\text{H}_2\text{SO}_4(\text{l})$  with  $\text{NH}_4\text{O}_4(\text{l})$  at  $18^\circ$  is expressed by the empirical equation,  $Q = 17860N/(N + 1.80)$  for values of  $N$  not exceeding 20. Calculate the heat-effect attending the addition to an infinite quantity of  $\text{H}_2\text{SO}_4.10\text{H}_2\text{O}$ , *a*, of  $1\text{H}_2\text{O}(\text{l})$ ; *b*, of  $1\text{H}_2\text{SO}_4(\text{l})$ . *Ans. a*, 231; *b*, 12820.

*\*Prob. 35. — a.* Determine with the aid of a plot of the heats of dilution given in the table of Art. 132 the heat-effect attending the addition of  $1\text{H}_2\text{O}(\text{l})$  to an infinite quantity of  $\text{ZnCl}_2.100\text{H}_2\text{O}$ . *b.* Derive a relation between the heat-effect attending the dissolving of  $1\text{ZnCl}_2(\text{s})$  in  $100\text{H}_2\text{O}(\text{l})$ , that attending the addition of  $100\text{H}_2\text{O}(\text{l})$  to an infinite quantity of a solution of the composition  $1\text{ZnCl}_2.100\text{H}_2\text{O}$ , and that attending the addition of  $1\text{ZnCl}_2(\text{s})$  to an infinite quantity of such a solution. *c.* Calculate the value of the last named heat-effect. *d.* Calculate the heat-content of  $1\text{ZnCl}_2$  in  $1\text{ZnCl}_2.100\text{H}_2\text{O}$ , taking that of  $1\text{ZnCl}_2(\text{s})$  equal to  $-97,300$  cal.

*\*Prob. 36. — The Effect of Temperature on Electrode-Potentials. —*  
*a.* Specify precisely the change in state whose heat-effect would be used in calculating the temperature-coefficient of the molal electrode-potential of  $\text{Zn}(\text{s})$ ,  $\text{Zn}^{++}$ . *b.* Calculate a value of this temperature-coefficient from the heat values found in Prob. 35, the heat-content ( $-22,000$  cal.) of  $1\text{HCl}(\text{g})$ , and its heat of dilution as given in Art. 132, considering for this purpose solutions with  $100\text{H}_2\text{O}$  per  $1\text{ZnCl}_2$ , or per  $1\text{HCl}$  as infinitely dilute.

## CHAPTER XIII

### \*SYSTEMIZATION OF FREE-ENERGY VALUES

---

**170. Importance of Systemizing Free-Energy Values.** — Since a knowledge of the changes in free energy attending chemical changes makes it possible to predict the direction in which they can take place and the conditions under which they are in equilibrium, the working-out of a complete system of free-energy values becomes an experimental problem of great chemical importance. The more general principles by which changes in free energy can be determined have already been fully considered in the preceding chapters. The purposes of this chapter are the direct application of these principles to the determination of free-energy values, and the presentation of certain conventions by which free-energy values can be systematized. These conventions will be first considered.

**171. Expression of Free-Energy Changes by Equations.** — Since the free energy of a substance is a quantity which, like its heat-content, is fully determined by its state, changes in free energy can be represented by equations corresponding in every respect to those used for expressing changes in heat-content; conventions being adopted for showing the state of the substance identical with those described in Art. 129. It will suffice to supplement the specifications of that article by the following statements.

Free-energy values are commonly expressed in calories on account of their close relations with heat-content data, which are commonly so expressed.

The pressure at which each substance exists must always be definite, since the free-energy is in general in a high degree dependent on the pressure. When not specified, the pressure is understood to be one atmosphere.

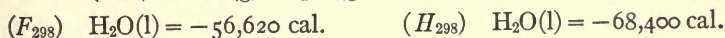
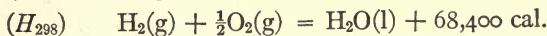
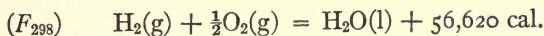
In correspondence with the convention as to the arbitrary zero-point of the heat-content scale, the free energy at any definite temperature of any definite quantity of a substance in any definite state is equal to the increase in free energy that attends the formation of the substance in that state out of the pure elementary substances at the same temperature, and at a pressure of one atmosphere, each elementary substance being in the state of aggregation that is the stable one

at this temperature and pressure. Thus the free energy of  $1\text{HI}(1\text{ atm.})$  at  $25^\circ$  refers to its formation from gaseous hydrogen and solid iodine at  $25^\circ$  and one atmosphere; but at  $400^\circ$  it refers to its formation from gaseous hydrogen and gaseous iodine at  $400^\circ$  and one atmosphere.

The free energy of a substance in a solution is understood to mean the increase in free energy attending the formation of the pure substance out of the elementary substances plus that attending the introduction of it into an infinite quantity of the solution under consideration. This free energy is indicated by attaching to the chemical formula a parenthesis showing the concentration or composition of the solution; for example,  $1\text{KCl}(\text{at } 0.1\text{ f.})$ ,  $1\text{H}_2\text{SO}_4(\text{in } \text{H}_2\text{SO}_4.10\text{H}_2\text{O})$ . The free energy of water in a solution is often conveniently referred to that of pure water (instead of to that of hydrogen and oxygen) as zero; and when so referred the symbol  $\text{Aq}$  (instead of  $\text{H}_2\text{O}$ ) is used; for example,  $5\text{Aq}(\text{in } \text{H}_2\text{SO}_4.10\text{H}_2\text{O})$ .

The free energy of an ion in aqueous solution is conveniently defined, in correspondence with the definition of electrode-potentials given in Art. 151, as the increase in free energy that attends the formation of the ion in solution at the specified concentration out of the elementary substance at one atmosphere, hydrogen-ion at 1 molal being formed at the same time out of hydrogen gas at one atmosphere. Thus the free energy of  $\text{Pb}^{++}(0.1\text{ m.})$  is equal to the increase in free energy that attends the reaction  $\text{Pb}(\text{s}) + 2\text{H}^+(1\text{ m.}) = \text{Pb}^{++}(0.1\text{ m.}) + \text{H}_2(1\text{ atm.})$ ; the free energy of  $\text{H}^+(1\text{ m.})$  as well as that of  $\text{H}_2(1\text{ atm.})$  being thereby arbitrarily assumed to be zero.

When necessary, equations expressing changes in free energy may be distinguished from those expressing changes in heat-content by prefixing to them the symbols ( $F$ ) and ( $H$ ), respectively; and the absolute temperature may be shown by attaching to this letter a subscript. For example:



Since the free energy of a substance at various small pressures or concentrations can be calculated, by the logarithmic expressions of Art. 137 and 138, from the free energy at any one definite small pressure or concentration, it suffices to determine and record the free energy

of each gaseous substance at one atmosphere and of each solute in each solvent at 1 molal. These standard values are, however, commonly so expressed as to represent the free energy of the substance at this pressure or concentration under the assumption that it behaves as a perfect gas or perfect solute up to this pressure or concentration; that is, they are calculated by the logarithmic equation from those determined at much smaller pressures or concentrations.

In the case of solutes so concentrated that they show large deviations from the behavior of perfect solutes the free energies must be determined at a series of concentrations, and these values must be separately recorded. Or, if preferred, the activity-coefficients corresponding to the free energies at various formalities of the substance may be calculated and recorded.

**172. Determination of the Free Energies of Substances.** — With the aid of the principles relating to free energy considered in chapters X, XI, and XII, and the conventions presented in the preceding article, the free energies of substances in their different states can be determined, as illustrated by the following problems.

*Prob. 1. — Free Energies of Elementary Substances in Different States.* With the aid of the principles of Arts. 137–139, calculate the free energy at 25° of, *a*,  $I_2(g)$  at 1 atm.; *b*,  $I_2$  (at 1 m. in  $H_2O$ ); and *c*,  $I_2$  (at 1 m. in  $CCl_4$ ). At 25° the vapor-pressure of pure iodine is 0.305 mm., its solubility in water is 0.00132 molal, and its distribution-ratio between carbon tetrachloride and water is 86.

*Prob. 2. — Free Energy of Solutes at High Concentrations.* — *a*. Calculate the free energy of 1NH<sub>3</sub> in a 8.6 n. solution in water at 25° from the following data at 25°. The free energy of 1NH<sub>3</sub>(g) is –4740 cal. The vapor-pressure of NH<sub>3</sub> from a 0.2 n. solution in water is 2.70 mm. The distribution-ratio of NH<sub>3</sub> between  $CCl_4$  and  $H_2O$  is 0.0040 when the NH<sub>3</sub> is 0.2 n. in the water, and 0.0086 when the NH<sub>3</sub> is 8.6 n. in the water. *b*. State the principles involved. *c*. State how the same free energy might be obtained from another kind of measurement with the 8.6 n. aqueous solution.

*Free Energies Derived from Electromotive Forces.* —

*Prob. 3.* — Calculate the free energy of 1HCl(g) at 25° from the facts that at 25° the cell  $H_2(1 \text{ atm.}), HCl(4 \text{ f.}), Cl_2(1 \text{ atm.})$  has an electromotive force of 1.262 volts, and that the vapor-pressure of the HCl in its 4 formal solution is 0.0182 mm. *Ans.* –22,800 cal.

*Prob. 4.* — Calculate the free energy of 1AgCl(s) at 25° from the molal electrode-potentials and the solubility of AgCl which is  $1.30 \times 10^{-6}$  formal at 25°. *Ans.* –26,200 cal.

*Prob. 5.* — Calculate the free energy of 1H<sub>2</sub>O(l) at 25° from the

electromotive force (0.926 volts) of the cell  $\text{H}_2(\text{g})$ ,  $\text{NaOH}(0.1 \text{ f.})$ ,  $\text{HgO}(\text{s}) + \text{Hg}(\text{l})$  and from the free energy ( $-13880 \text{ cal.}$ ) of  $1\text{HgO}(\text{s})$  at  $25^\circ$ . *Ans.*  $-56,600 \text{ cal.}$

*Prob. 6.* — Calculate the free energy of  $1\text{Ag}_2\text{O}(\text{s})$  at  $25^\circ$ . The electromotive force of the cell  $\text{H}_2(\text{g})$ ,  $\text{KOH}(0.1 \text{ f.})$ ,  $\text{Ag}_2\text{O}(\text{s}) + \text{Ag}(\text{s})$  is  $1.172 \text{ volt}$  at  $25^\circ$ . *Ans.*  $-2500 \text{ cal.}$

*Prob. 7.* — Formulate the free energy equation which can be derived from the molal electrode-potential of, *a*,  $\text{Cl}_2(\text{g})$ ,  $\text{Cl}^-$ , and *b*,  $\text{O}_2(\text{g})$ ,  $\text{OH}^-$ . Find the free energy at  $25^\circ$ , *c*, of  $\text{Cl}^-$  ( $1 \text{ m.}$ ), and *d*, of  $\text{OH}^-$  ( $1 \text{ m.}$ ). *Ans.* *c*,  $-31,400 \text{ cal.}$ ; *d*,  $-37,400 \text{ cal.}$

*Free Energies Derived from Equilibrium Measurements.* —

*Prob. 8.* — Calculate the free energy of  $1\text{NO}(\text{g})$  at  $1957^\circ$  from the data of Prob. 21, Art. 167. *Ans.*  $13,700 \text{ cal.}$

*Prob. 9.* — Calculate the free energy of  $1\text{HgO}(\text{s})$  at  $357^\circ$  from its dissociation pressure at  $357^\circ$  found in Prob. 24, Art. 167. *Ans.*  $-5700 \text{ cal.}$

*The Free Energy of a Substance at One Temperature Derived from its Free Energy at Another Temperature.* —

*Prob. 10.* — With the aid of the free-energy equation of Art. 166 calculate the free energy of  $1\text{NO}(\text{g})$  at  $25^\circ$  from its free energy at  $1957^\circ$  found in Prob. 8 and from the heat data of Prob. 21 of Art. 167. *Ans.*  $20,500 \text{ cal.}$

*Prob. 11.* — Calculate the free energy of  $1\text{HgO}(\text{s})$  at  $25^\circ$  from its free energy at  $357^\circ$  found in Prob. 9 and from the heat data of Prob. 24, Art. 167, considering the heat of dissociation of solid mercuric oxide into liquid mercury and oxygen to be a linear function of the temperature between  $25^\circ$  and  $357^\circ$ . *Ans.*  $-14,100 \text{ cal.}$

*Prob. 12.* — Calculate the free energy at  $25^\circ$  of  $1 \text{ at. wt.}$  of monoclinic sulfur from the facts that its conversion into rhombic sulfur at its transition-point ( $95.5^\circ$ ) is attended by a heat-evolution of  $105 \text{ cal.}$  and that the atomic heat-capacities of the monoclinic and rhombic forms are  $6.0$  and  $5.7 \text{ cal. per degree.}$  Tabulate this result with that obtained in Prob. 19 of Art. 139.

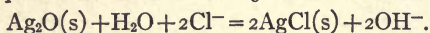
*Prob. 13.* — *Derivation of Free Energies from Original Data.* — By a thorough examination of the chemical literature to find all the data bearing on the problem and by a critical consideration of these data derive the best values of the free energy at  $25^\circ$ , and of a function expressing its change with the temperature, for one of the following solid substances (assigned by the instructor):  $\text{Ag}_2\text{O}$ ,  $\text{HgO}$ ,  $\text{AgCl}$ ,  $\text{PbCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ ,  $\text{HgCl}_2$ ,  $\text{CuCl}$ ,  $\text{AgI}$ , etc.

**173. The Equilibrium-Conditions of Chemical Reactions Derived from the Free Energies of the Substances Involved.** — When values of the free energies of substances have been once determined by the methods already described, these values can be employed, conversely, for calculating the free-energy decrease attending chemical changes

and their equilibrium-constants, as in the following problems. From this fact arises the great importance, already referred to, of a complete, systematic knowledge of the free energies of substances.

*The Equilibrium-Constants of Chemical Reactions Calculated from the Free Energies of the Separate Substances. —*

*Prob. 14. — a.* Calculate from the free energy values already considered the equilibrium-constant at  $25^{\circ}$  of the reaction:



*b.* State what mixture would finally result if  $1\text{Ag}_2\text{O}(\text{s})$  were treated at  $25^{\circ}$  with 1 l. of 0.1 f. NaCl solution.

*Prob. 15. — a.* Calculate from the free energy values the equilibrium-constant of the reaction  $4\text{HCl}(\text{g}) + \text{O}_2(\text{g}) = 2\text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$  at  $25^{\circ}$ .

*b.* Calculate the mol-percents of chlorine and oxygen in the gas which at 1 atm. and  $25^{\circ}$  would escape from a 4 f. HCl solution if oxygen at 1 atm. were passed through it in contact with a catalyst so that equilibrium was established. At  $25^{\circ}$  in 4 f. HCl solution the vapor-pressures of the water and HCl are 19.6 mm. and 0.0182 mm., respectively.

*Ans. a,*  $1.3 \times 10^{13}$ ; *b,*  $\text{Cl}_2$ , 7.2%,  $\text{O}_2$ , 90%.

---

# NOTATION

$a$  activity; area.  
 $a, b$  van der Waals constants.  
 $c$  molal concentration; molarity.  
 $d$  density.  
 $d$  differential.  
 $e$  base of natural logarithms.  
 $f$  force.  
 $g$  gravity-acceleration.  
 $h$  height; hydrolysis.  
 $i$  mol-number.  
 $k$  kinetic-energy constant.  
 $k$  specific reaction-rate.  
 $l$  distance; length.  
 $m$  mass.

$n$  number.  
 $n$  number of molecules.  
 $\bar{n}$  number of molecules in one mol.  
 $p$  pressure.  
 $r$  radius.  
 $s$  solubility.  
 $t$  time.  
 $t$  centigrade temperature.  
 $u$  velocity.  
 $v$  volume.  
 $\bar{v}$  specific volume.  
 $\bar{v}$  molal volume.  
 $x$  mol-fraction.  
 $x, y, z$  coördinates.

$A$  atomic weight; work-content  
 $A, B$  constants.  
 $C$  heat-capacity.  
 $\bar{C}$  specific heat-capacity.  
 $\bar{C}$  molal heat-capacity.  
 $E$  energy.  
 $F$  free energy.  
 $H$  heat-content.  
 $K$  equilibrium-constant.  
 $K$  kinetic energy.

$M$  molecular weight.  
 $N$  number of mols.  
 $P$  osmotic pressure.  
 $P$  probability.  
 $Q$  heat evolved.  
 $R$  gas-constant.  
 $S$  entropy.  
 $T$  absolute temperature.  
 $U$  energy-content.  
 $W$  work.

$C$  normal concentration; normality.  
 $E$  electromotive force.  
 $E$  electrode-potential.  
 $\bar{E}$  molal electrode-potential.  
 $F$  faraday.  
 $I$  current-strength.  
 $L$  conductance.

$\bar{L}$  specific conductance.  
 $N$  number of equivalents or faradays.  
 $Q$  quantity of electricity.  
 $R$  resistance.  
 $T$  transference number.  
 $U$  ion-mobility.  
 $V$  potential.

$\alpha$  activity-coefficient.  
 $\alpha, \beta$  coefficients.  
 $\gamma$  dissociation or ionization.  
 $\Delta$  increment.  
 $\eta$  viscosity.

$\lambda$  wave-length.  
 $\Lambda$  equivalent conductance.  
 $\nu$  frequency.  
 $\pi$  circumference-diameter ratio.  
 $\Sigma$  summation.



# INDEX

In this index formal statements of laws or principles and their formulations in equations are itemized under the heading "laws, principles, fundamental equations." Definitions of "concepts, properties, and fundamental constants," values of the "constants of chemical substances," and definitions and values of "units" are entered under these headings, respectively.

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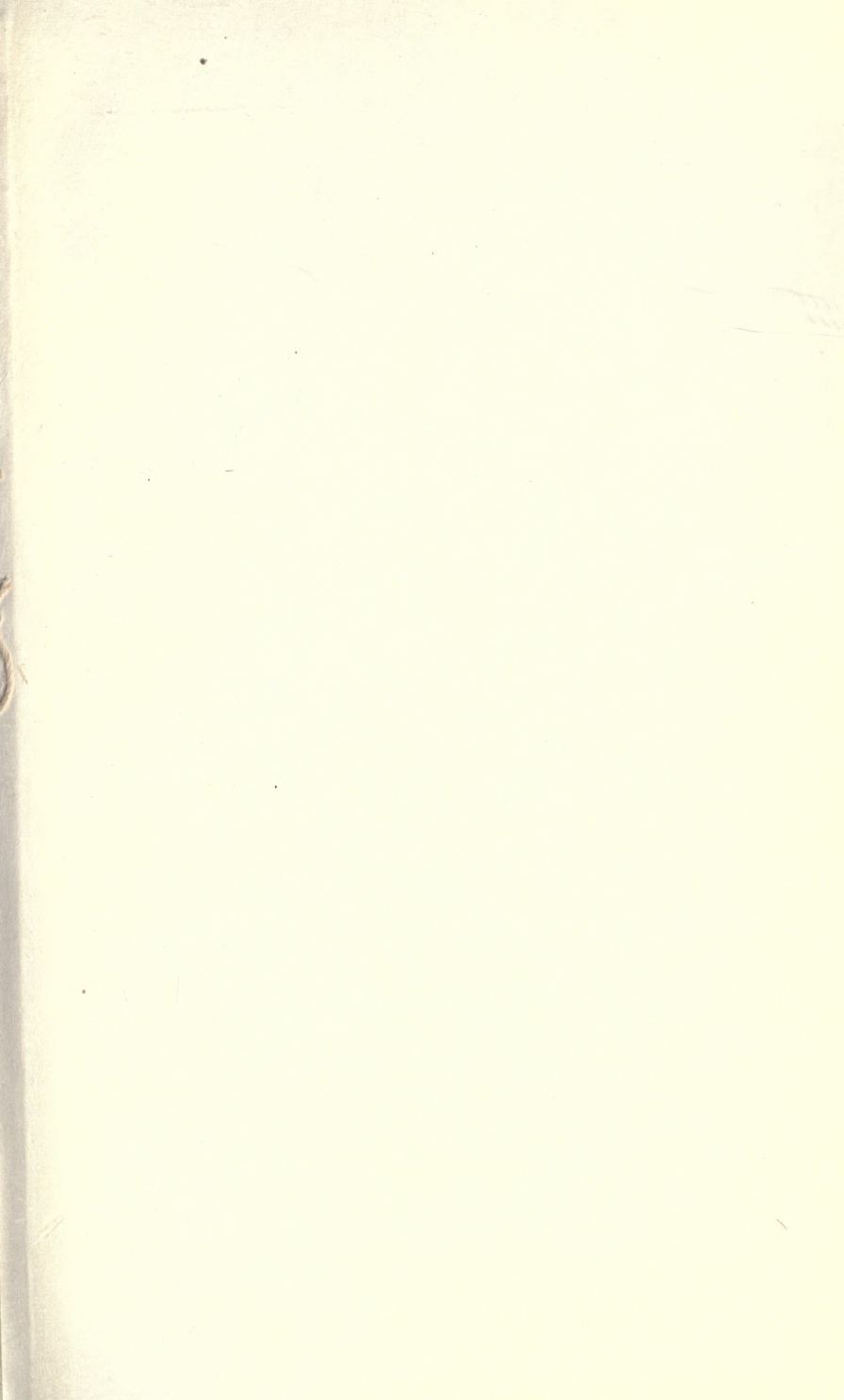
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